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Salinity Change in Alligator Harbor and Ochlockonee Bay, Florida[1]

Takashi ICHIYE[2], Meredith L. JONES[3], Neil C. HULINGS[4], and F. C. W. OLSON[5]

Abstract: The hydrographic data of two shallow bays on the northern Gulf coast of Florida are analyzed with emphasis on salinity variation. Alligator Harbor, a neutral bay, has an almost uniform vertical salinity distribution. The highest salinity was observed in the early flood stage at the inner end, while salinity variation is irregular at the mouth and in the central part of the bay. In Ochlocknee Bay, on the other hand, the surface salinity changes by more than 20‰ during one tidal cycle. In flood stages particularly, a salt wedge is formed in a deep channel.

Some theoretical models about advective change of salinity due to variable currents are proposed in order to explain the observed data. Vertical stability of water in these bays is also discussed.

1. Introduction

The hydrography of estuaries is one of the most challenging problems in physical oceanography. Surprisingly few studies of estuaries have been made though these areas are frequently of great economic value. The physical and biological processes of these areas are very complex and require specialized instruments for obtaining data concerning them.

The present study is based on various kinds of observations made at Alligator Harbor and Ochlockonee Bay on the northern coast of the Gulf of Mexico in Florida (Fig. 1). These bays are relatively shallow and are influenced to a greater or lesser extent by tidal currents. Although they are near each other, their geometrical, physical and biological properties are different. Therefore, it will be more informative to describe them comparatively than to discuss them separately in detail.

Rather than describing the general hydrography of these bays, this report will be concerned with the problem of salinity fluctuation in relation with tidal stages. Salinity fluctuations will serve to illustrate hydrographic characteristics quite well. In addition, information concerning diffusion, which is important as regards physical oceanography, can be obtained from these data of salinity change.

Fig. 1. Chart of Alligator Harbor and Ochlockonee Bay from Chart No. 1261 "Apalachee Bay" of U. S. Coast and Geodetic Survey. (Broken and chain lines indicate depths of 6 and 12 feet, respectively. The area marked "A" in an inserted map is the location of the bays).

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2. Alligator Harbor

Alligator Harbor is about 1¼ miles wide, 4 miles long and the mean depth at low water is about 4 feet (Fig. 1, taken from U. S. Coast and Geodetic Survey Chart No. 1261-Apalachee Bay). It is the site of the Marine Laboratory of Oceanographic Institute of the Florida State University and thus, sporadic hydrographic and biological studies in this area have been carried out since 1951. Some of the results are described in the report of OLSON (1955).

Composite charts of tidal currents based on the data of 3, 9, and 10 May 1952 and 11 April 1953 are shown in Fig. 2, (1) and (2). The currents are strongest at the mouth and decrease towards the inner end. Current direction is almost uniform vertically, although speed decreases slightly towards the bottom, because the bay is shallow and there is no conspicuous inflow of drainage from adjacent areas.

Simultaneous observations of salinity, currents and tides on 11 April 1953 are shown in Fig. 2, (3) and (4). Location of the stations occupied is indicated in Fig. 2, (1). Water sampling and measurements of surface currents at three stations were taken every twenty minutes.

The salinity change at stations A and B is rather irregular. The periods of about 2 hours in salinity fluctuation observed at station A seem to correspond to those of the seiches of the bay (ICHIYE and DOWLING, 1960). The station C shows the largest amplitude of salinity fluctuation among the three stations. Here there appears to be a correlation of salinity with tidal period, there being higher salinities during high water. Such characteristics can be explained from the advection theory (Section 4 below). In addition Fig. 2 (3) suggests that stratification of salinity is slight at the three stations.

In Fig. 2 (5) salinity and currents observed by RICHARD WALLER (personal file) at two narrow passes on April 24 in 1960 are plotted. The measurements were done at one hour intervals. Current speeds at these passes are higher than at other stations described above. At Station I, main directions of flood and ebb currents are north and south, respectively. Salinity was lowest at the slack from flood to ebb and highest

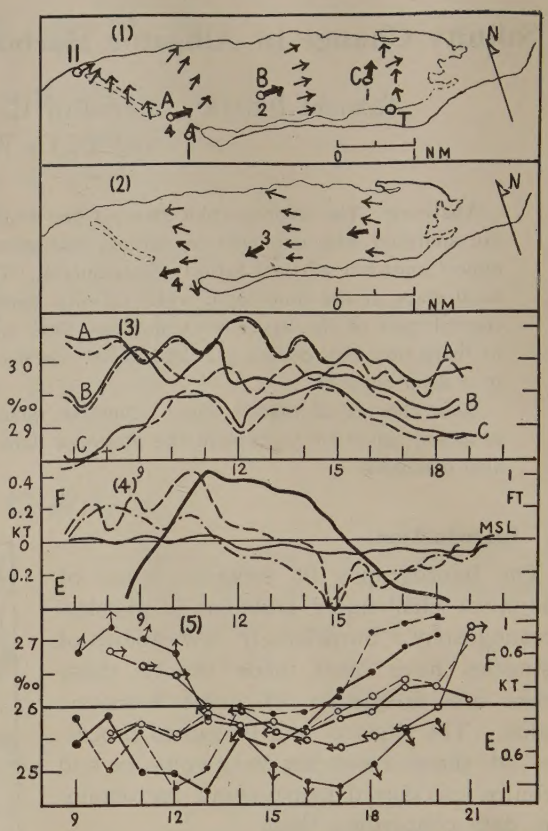

Fig. 2. Currents and salinity change at Alligator Harbor. (1) Surface current at the peak of flood stage. (Thick arrows and figures indicate direction and speed in 0.1 kt, fine arrows indicate direction only; A, B, C, I, II and T are hydrographic stations and the tidal station, respectively.) (2) Surface currents at the peak of ebb stage. (3) Change of salinity at St. A, B and C observed on 11 April, 1953. (Broken lines are for surface data and full lines for bottom data.) (4) Change of currents (thin lines; broken line for A, chain line for B, full line for C) and tidal height at St. T (thick, full line). F and E mean flood and ebb stage, respectively. (5) Change of salinity and surface currents at St. I and II observed on 24 April, 1960. (Closed circles are for St. I and open circles for St. II; full lines for surface salinity, broken lines for bottom salinity; arrows with circles indicate direction and speed of currents.)

at the slack from ebb to flood, in agreement with the theory derived in Section 4.

The horizontal gradient of salinity distribution is usually small. The bay is classified as neutral bay (PRITCHARD, 1952). Three examples of surface salinity distributions are shown in Fig. 3. Normal conditions are

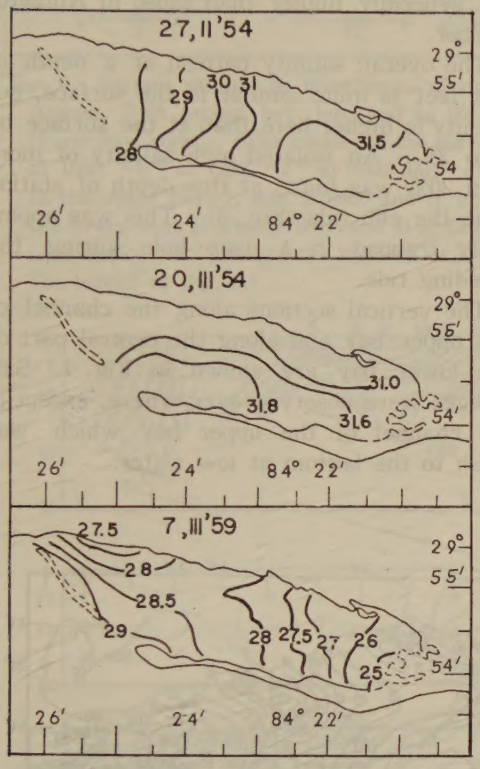

Fig. 3. Examples of salinity distributions at the surface of Alligator Harbor (in ‰). The top, middle and bottom chart are numbered as (1), (2) and (3), respectively.

either higher salinity towards the mouth as in Fig. 3 (3) or a negligible horizontal gradient as in Fig. 3 (2). The salinity distribution of Fig. 3 (1) shows a decrease towards the mouth of the bay due to fresh water coming from Ochlockonee Bay.

3. Ochlockonee Bay

Ochlockonee Bay is also a small tidal estuary of about 1¼ miles width and 5 miles length. It is located to the north of Alligator Harbor (Fig. 1). The bay is divided into an upper and a lower part by a bridge. The lower bay is relatively deep, with the deepest part in the middle, while the upper bay is less than 4 feet, except for narrow channels on both sides, which are the channels of two rivers, the Sopchoppy and the Ochlockonee. There is less hydrographic data for this bay

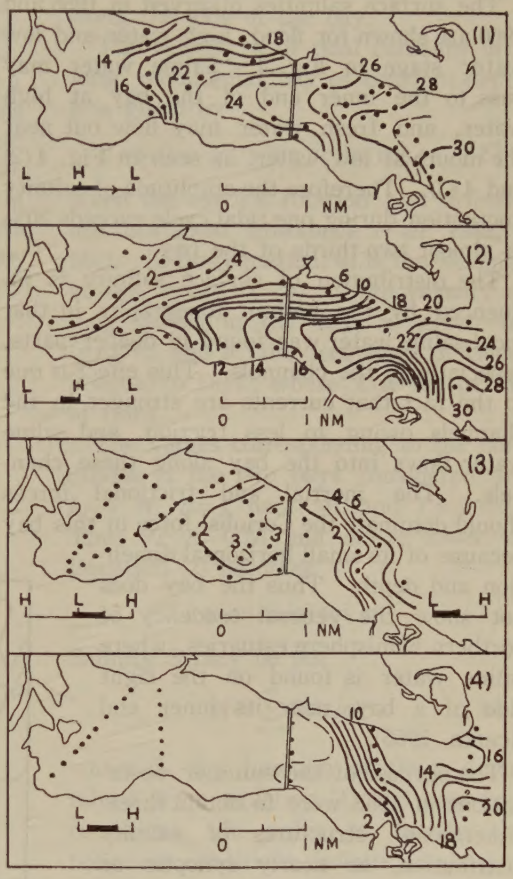

Fig. 4. Surface salinity in Ochlockonee Bay. (1) Observed from 1025 to 1355 on 24 March, 1956. L (for low water) was at 0718 and H (for high water) was at 1334. The block between L and H indicates a time interval, during which the survey was carried out. (2) Observed from 1037 to 1330 on 5 May, 1956 (L at 0437 and at 1730, H at 1105). (3) Observed from 1015 to 1330 on 17 March, 1956 (upper bay, left) and from 1010 to 1320 on 25 July, 1956 (lower bay, right). (On March 17, L was at 1051, H at 1704. On July 25, L was at 0948 and H at 1545.) (4) Observed from 1100 to 1425 on 11 April, 1959. (L was at 0957, H at 1549).

than for Alligator Harbor, and more data would be extremely interesting because of the remarkable fluctuations of salinity and strong horizontal gradients of the water masses. Most data discussed here were obtained by HULINGS during 1956, by HULINGS and ICHIYE during the summer of 1958 and by Thomas HOPKINS (personal file) in 1960.

The surface salinities observed in 1956 and 1960 are shown for flood, high water and low water stage in Fig. 4. Saline water may pass to the inner end of the bay at high water, and fresh water may flow out near the mouth at low water, as seen in Fig. 4 (2) and 4 (3). Therefore the amplitude of salinity fluctuation during one tidal cycle exceeds 20‰ in almost two-thirds of the bay.

The distribution of surface salinity is influenced by the bottom topography in that most saline water was found in deeper parts, especially in the channels. This effect is due to the fact that currents are stronger in the channels owing to less friction, and saline water flows into the bay along these channels. The inertial and frictional forces should dominate the Coriolis' force in this bay because of its small horizontal dimension and depth. Thus the bay does not show the general tendency of northern hemisphere estuaries, where saline water is found on the right side of a bay, near its inner end (ICHIYE, 1955).

The purpose of the summer observations of 1958 were to obtain three-dimensional structures of salinity distribution, as nearly synoptic as possible. The distributions of surface salinity are shown for high water and ebb in Figs. 5 and 6, respectively, and they are quite similar to those of Fig. 4. Salinity of the lower bay in Fig. 5 did not reach the highest values which were obtained at high water, as seen in the salinity distribution of Fig. 4 (2). In Fig. 6 a foam line is indicated which was observed along the boundary between fresh and saline water in the lower bay. This bay is locally well-known for foam lines. It was also observed, in this case, that the surface of the fresh water on the one side of the foam line was smooth, while the surface of the salt water on the other was covered with ripples.

Surface currents measured in this survey are also plotted in Figs. 5 and 6. The velocities are particularly high in the channels and are generally higher than those in Alligator Harbor.

The overall salinity pattern at a depth of five feet is quite similar to the surface, but salinity is higher here than at the surface by 1 to 3‰. An isolated high salinity of more than 20‰ was found at this depth of station c at the ebb tide (Fig. 6). This was apparently trapped in a deep hole during the receding tide.

The vertical sections along the channel of the upper bay and along the central part of the lower bay are shown in Fig. 7. Salt wedges were observed everywhere, except in the channel of the upper bay which was fresh to the bottom at low water.

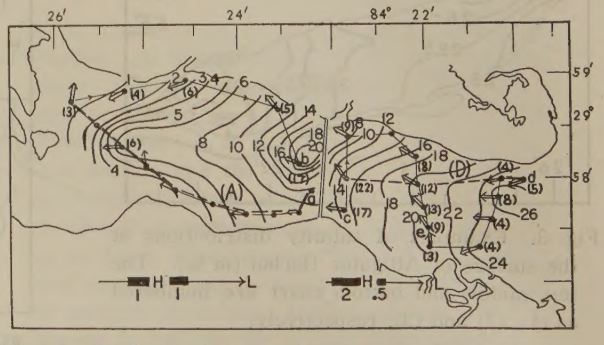

Fig. 5. Surface salinity at high water observed on 30 July, 1958 (upper bay, left) and on 1 August, 1958 (lower bay, right). The courses of the surveys: "a" at 1230, "b" at 1442, "c" at 1335 and "d" at 1545. In the upper bay, H was at 1357 and L at 2106. In the lower bay, H was at 1516 and L at 2206. Arrows indicate current directions and figures in parenthesis indicate the velocity in one tenth of knot. The broken lines indicate the sections, vertical profiles of which are plotted in Fig. 7. At stations "b" and "e" Richardson number is computed and is tabulated in Table 2. Figures beside the block indicate a duration of the surveys in hours.)

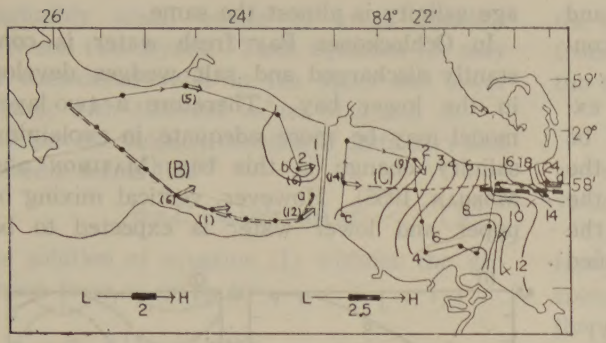

Fig. 6. Surface salinity in flood stage observed on 1 August, 1958 (upper bay, left) and on 30 July, 1958 (lower bay, right). (The courses of the surveys: "a" at 1020, "b" at 1228, "c" at 0907 and "d" at 1139. In the upper bay, L was at 0930 and H at 1516. In the lower bay, L was at 0817 and H at 1357. Blocks near station "d" indicate the location of a foam line. See legend of Fig. 5.)

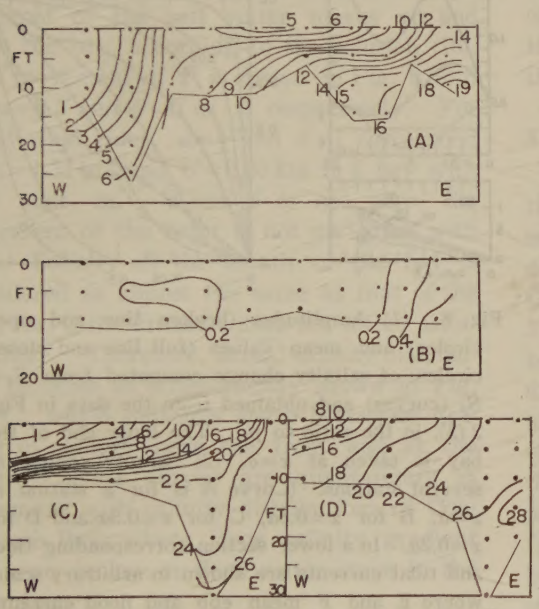

Fig. 7. Vertical profiles of salinity. (See Figs. 5 and 6 for locations of the sections. Sections (A) and (C) were observed on 30 July and sections (B) and (D) on 1 August, 1958).

4. A mathematical model of salinity fluctuation in a vertically homogeneous estuary

In a shallow estuary, such as Alligator Harbor, salinity is almost homogeneous vertically. Salinity change in such an estuary is caused primarily by advection of tidal currents and horizontal diffusion. A theorical model of this salinity change may be derived, assuming one-dimensional distribution. The equation for conservation of salinity in unit volume is given by

$$\partial S/\partial t + u\partial S/\partial x = A\partial^2 S/\partial x^2 \quad (1)$$

where S is the salinity, u is horizontal velocity, A is horizontal eddy diffusivity and x is the distance from the inner end along the axis of the bay.

The velocity u of tidal currents in a long, rectangular bay of constant depth h is given by

$$u = u_0(\sin \sigma c^{-1}x/\sin \sigma c^{-1}a)\cos \sigma t \quad (2)$$

when the earth's rotation and friction are neglected (Sverdrup *et al*, 1942, p 552). In this equation, u_0 is the velocity at the mouth ($x=a$): c, the velocity of long waves in the bay, is given by $(gh)^{1/2}$; and σ, the frequency of tides, is equal to $2\pi/T$, where T is the period of tides.

The values corresponding to the conditions of the two bays considered are $h=5$ ft, $a=4$ naut. m. and $T=\frac{1}{2}$ day. Thus $\sigma c^{-1}a=0.28$ and $\sin \sigma c^{-1}a \approx \sigma c^{-1}a$. Equation (2) becomes

$$u = u_0(x/a)\cos \sigma t \quad (3)$$

Salinity S may be put

$$S = \sum_{n=0}^{\infty} S_n(x/a)^n \quad (4)$$

where S_n is a function of time, determined from equation (1) and boundary conditions. In order to satisfy the boundary conditions, infinite numbers of S_n are generally needed. In this paper, instead of implying specific boundary conditions, S is assumed to be a quadratic function of x/a. The integration constants may be adjusted so as to satisfy the boundary conditions as nearly as possible.

Substituting (4) into (1) and equating coefficients of the same powers of x/a on both sides of (1), we have

$$\partial S_0/\partial t = AS_2a^{-2} \quad (5)$$

$$S_1 = p_1 \exp(-\alpha \sin \sigma t) \quad (6)$$

$$S_2 = p_2 \exp(-2\alpha \sin \sigma t) \quad (7)$$

in which $\alpha=u_0(a\sigma)^{-1}$. The constants p_1 and p_2 can be determined from the boundary conditions.

Since $\alpha=0.19$ for $u_0=0.4$ kts, the exponential functions of (6) and (7) may be approximated by the expansion about the arguments up to the first power. Then the condition that salinity change is small at the mouth as seen in Figs. 2 (3) and 4 is satisfied by taking.

$$p_1=-2p_2 \qquad (8)$$

Eddy diffusivity is effective only when S includes term S_n, with $n\geqslant 2$. When the salinity, averaged over a period of time decreases towards the inner end of the bay, as is usually the case, p_1 positive. Then equations (5) and (8) indicate that salinity decreases steadily everywhere in the bay. The value of A becomes 6×10^5 cm^2/sec, when it is determined from the 4/3-power law, by taking the scale of turbulence equal to a, the length of the bay (Ichiye and Olson, 1960). From equation (5), the decrease of S during half a day is equal to $0.82\times10^{-7}\,p_1 A$, or $0.05\times p_1$, which is almost negligible. Thus the solution consisting of S_1 and S_2 only may represent the salinity distribution during a few cycles of semi-diurnal tides.

The time-averaged salinity and the amplitudes of fluctuation in a rectangular bay, computed by the sum of S_1 and S_2 for $\alpha=0.19$, are plotted in Fig. 8 (1). The observed values determined from the data at stations A, B and C of Alligator Harbor in Fig. 2 (3) are also plotted in this figure, which shows a good agreement between theoretical and observed values.

In fig. 8 (2) theoretical curves of salinity change at several stations are plotted. The highest salinity at each station is attained at high water or at the end of flood tides, except at the mouth. This is again in agreement with the salinity change observed at Alligator Harbor and Ochlockonee Bay.

The amplitude of salinity change increases with the velocity, as seen in the definition of α. When u_0 is taken as 2 kts, for example, the amplitude in the middle of the bay becomes five times larger than that shown in Fig. 8 (1), while the distribution of the average salinity is almost the same.

In Ochlockonee Bay fresh water is constantly discharged and salt wedges develop in the lower bay. Therefore a two-layer model may be more adequate in explaining salinity change in this bay (Maximon and Morgan, 1955). However, vertical mixing of upper and lower water is expected to be

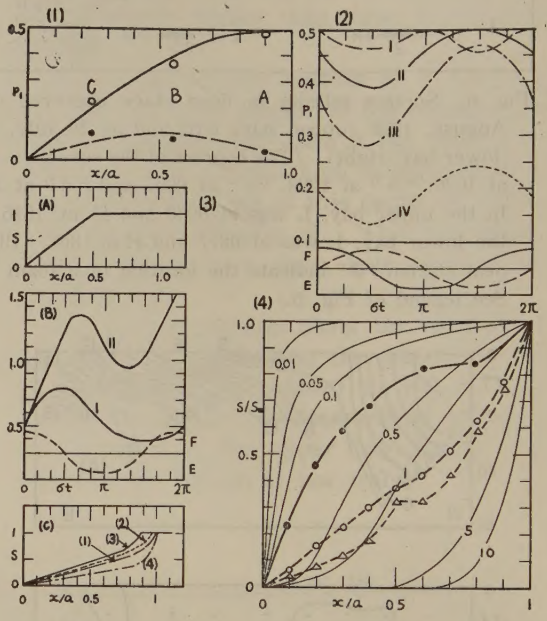

Fig. 8. (1) Amplitudes (broken line and open circles) and mean values (full line and closed circles) of salinity change computed from S_1+S_2 (curves) and obtained from the data in Fig. 2 (3), in the ratio to p_1. The inner end of the bay is taken at $x=o$. (2) Salinity change at several stations. (Curve A is for a station at $x=a$, B for $x=0.8a$, C for $x=0.5a$ and D for $x=0.2a$. In a lower section corresponding tides and tidal currents are shown in arbitrary scale, where E and F mean ebb and flood current.) (3) (A) Initial distribution of salinity. (B) Location of the point P during one tidal cycle. (Full line is for $\beta=0.25$ and broken line for $\beta=0$.) (C) Schematical distributions of salinity at $\tau=\pi/2$, π, $3\pi/2$ and 2π for $\beta=0.25$ (4) Longitudinal distributions of averaged salinity. (Closed circles are for Alligator Harbor from the data in Fig. 3 (3). Open circles and triangles are for Ochlockonee Bay: the circles are from the average of four surveys in Figs. 4 and the triangles are from the average of two surveys in summer of 1958 of Fig. 5 and 6. Thin lines are theoretical curves for different values of F.)

negligibly small owing to great stability between two layers. Then equation (3) may be considered valid in the upper and lower layers, with different values of u and A.

When the velocity consists of stationary and periodic terms like

$$u=U+u_0(x/a)\cos\sigma t \qquad (9)$$

the solution of equation (1) without the diffusion term is given by

$$S=f\left\{(x/a)\exp(-\alpha\sin\tau)-\beta\int_0^{\tau}\exp(-\alpha\sin\tau)d\tau\right\} \qquad (10)$$

in which $\tau=\sigma t$, $\beta=U(a\sigma)^{-1}$ and the function $f(x/a)$ expresses the distribution of salinity at $t=0$. When the initial distribution is represented by the curve shown in Fig. 8 (3)-A, the front of the salt water moves up and down the bay, according to the solution (10). This movement of P is shown in Fig. 8 (3)-B for $\alpha=0.5$ and $\beta=0$ or $\frac{1}{4}$, respectively. For semidiurnal tides, $\alpha=\frac{1}{2}$ and $\beta=\frac{1}{4}$ correspond to $u_0=1.31$ kts and $U=0.66$ kts in a bay with $a=5$ naut. m. When β is not zero, the movement of the front is not periodical with time. Salinity off the mouth of the bay is considered as almost the same as that of the open sea, if the drainage does not affect salinity there. Therefore, actual salinity distribution becomes as schematically shown in Fig. 8 (3)-C, which indicates sharp horizontal gradient of salinity near the front and at the mouth. These curves are qualitatively in agreement with salinity distributions of Ochlockonee Bay, where large salinity gradient was seen in low or flood water stage in the lower bay.

Arons and Stommel (1952) derived the relation between the longitudinal distribution of average salinity and flush number in a shallow estuary. The flush number F is defined as $vh^2/(2B\zeta^2a\sigma)$ in which v is the velocity of river flow, ζ is the amplitude of tides, B is a non-dimensional constant and other notations have the same meaning as before. When geometrical conditions of a bay are the same, a larger flow of fresh water leads to a larger flush number. In Fig. 8 (4), the ratio of salinity S to its maximum at the mouth S_m in the two bays are plotted against the distance from the inner end. The curves representing the theoretical relation

$$S/S_m=\exp\{F(1-a/x)\} \qquad (11)$$

are also plotted in this figure for different values of F.

The curve for Alligator Harbor obtained from the data of May, 1959 (Fig. 3) corresponds to a smaller value of flush number than those for Ochlockonee Bay and suggests us that the inflow of fresh water is less in the former than in the latter. One curve for Ochlockonee Bay obtained from the average salinity of four surveys (Fig. 4) corresponds to a slightly smaller flush number than the other curve obtained from two successive surveys in the summer of 1958 (Figs. 5 and 6). This indicates again that the average inflow of fresh water of different years and seasons is less than that of one particular period of time.

5. Vertical stability

In order to study, statistically, the distribution of stability in an estuary, the maximum salinity difference per 5 feet of depth has been determined at each station from the data of Ochlockonee Bay in the summer of 1958 (Figs. 5 and 6). The frequency distribution of numbers of stations is tabulated against salinity differences in Table 1, for the upper and lower bay and for ebb and flood tide. Most stations have a maximum difference of less than 2‰, though this bay is defined as an positive estuary. This is due to the fact that fresh water fills the upper bay almost to the bottom at the ebb tide. If we discard the stations of the ebb tide in the upper bay, the maximum frequency will be in the range of differences of 6 to 8‰.

The criterion of the effect of stability on fluid motion is represented by Richardson number Ri, which is defined by

$$Ri=(gd\sigma_t/dz\times10^{-3})/(du/dz)^2 \qquad (12)$$

where σ_t means density *in situ* (Dietrich, 1957). In order to compute it from the data, simultaneous observations of currents and density are necessary. Such data are given by those of stations b and e (Fig. 5). Direc-

Table 1. Frequency of stations against the maximum salinity difference per 5 feet depth. (Ochlockonee Bay. Based on the surveys of July 30 and August 1 of 1958.)

Group of Sts.	Maximum difference per 5 feet (‰)									
	0-2	2-4	4-6	6-8	8-10	10-12	12-14	14-16	16-18	18-20
Ebb Tide *Lower bay*	3	0	1	3	4	0	2	0	0	2
Flood Tide *Lower bay*	3	4	1	2	0	1	0	1	0	0
Ebb Tide *Upper bay*	13	0	1	0	0	0	0	0	0	0
Flood Tide *Upper bay*	7	1	4	2	0	0	0	0	0	0
Total	26	5	7	7	4	1	2	1	0	2

tions of surface currents at these stations are also shown in Fig. 5. In Table 2, values of sigma-*t*, velocity and *Ri* are tabulated at each five feet for these stations. The values of *Ri* obtained are smaller than those computed

Table 2. Velocity *u* (cm/sec), sigma-*t* and *Ri* at two stations observed on August 1, 1958.

St. b				St. e		
z(ft)	*u*	σ_t	*Ri*	*u*	σ_t	*Ri*
0	86	1.8	1.4	49	4.5	2.3
5	75	3.0	1.6	30	10.4	1.3
10	60	7.4	0.9	5	15.6	
15	34	12.1				

by TAYLOR (1931) from the data of a Norwegian fjord. TOWNSEND (1957) determined a critical RICHARDSON number of 0.5 as the upper limit for maintaining turbulence in a stratified flow. The values of *Ri* at these stations are larger than this critical value. The stability condition at these stations is typical for the seaward end of the fresh-water tongue or at the landward end of the salt-water wedge. Therefore, it may be concluded that vertical stability in Ochlockonee Bay is so strong in the regions of contact of fresh and salt water that vertical mixing is negligible during one tidal cycle.

6. Concluding remarks

The present study is incomplete as far as the data are concerned, because all the data used for this study, except those of Ochlockonee Bay in the summer of 1958, were not obatined for this specific purpose and thus collected at random, so to speak, in time and space. It is desirable to develop three approaches of research for studying salinity change in those bays. The first and most basic approach is to know processes of turbulent diffusion which is a main cause of mixing of fresh and salt water, by recording salinity and velocity fluctuations continuously. The second approach is to obtain synoptic pictures of salinity distribution at successive stages of tides by using more than two boats simultaneously. This is particularly important in a bay like Ochlockonee Bay, where salinity changes conspicuously both in time and space. The third approach is to obtain daily salinity data for a long period of time at a few stations in a bay like Alligator Harbor, where salinity change during one tidal cycle may be small but there is quite a large day-to-day change.

Acknowledgement

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Geochemical Studies on Recent Sediments—IV. Chlorophyll Degradation Products in Surface Muds from the Kagoshima Bay in Japan*

Yukio SUGIMURA**

Abstract: Sediments from the basin of Kagoshima Bay have been examined for acetone-soluble chlorophyll derivatives which are regarded as the source material of the major porphyrins in crude oils

For quantitative estimation, the pigments in sediment extracts were calculated as pheophytin equivalent which is believed to be the most abundant of several similar one.

13 surface sediment samples were examined. Determination were made for pigment, nitrogen, and carbon. That the pigment ranges from 6 to 53 ppm based on dry sediment and varies from 580 to 2820 ppm based on organic matter.

Chlorophyll derivatives in basin sediments which compared with the pigment content of phytoplankton are preserved as much as 10% or less in the surface zone of mud.

This method appear preferable to the previous acetone-chloroform system of pigment extraction, because of the easy care of extraction procedure.

1. Introduction

The pioneering work of TREIBS (1934, 1936) in the thirties established the presence of porphyrins in various natural fossil sources. Recently, ORR (1958) VALLENTYNE (1955) and other workers have extended the studies of these lipids in recent marine or lacustrine sediments.

The gross aspects of present knowledge are briefly summarised as follows. 1. Porphyrins are widespread in fossil organic materials but are much more abundant in petroleum and oil shales than in coals. 2. The organic structure of the porphyrins suggests that they are derived from chlorophyll, hemin and structually related compounds. Chlorophyll derivatives are more abundant than those of hemin. 3. Porphyrins are present in fossil fuels in the form of metal complexes, but the material containing metals are not those originally present in common plant and animal pigments. Instead of magnesium and iron which are originally present in these pigments, vanadium and nickel are the abundant metals.

Very little is known about these organic matters of their abundance and behavior in mud from various sedimentary environments. Therefore it was worthwhile to investigate this problem in the surface muds of Kagoshima Bay, which is located in southernmost of Kyushu Island, Japan.

2. Materials and Methods

Sediment samples. Marine sediment samples were collected in the bay of Kagoshima in basin areas. Water depth ranges from 80 to 200 meters for these basin sediments. Oxygen is saturated near the surface, and decreases with depths. In order to the rapid oxidation of easily oxidised organic matter falling through water, oxygen have been consumed near the basin floor. Samples were bottled upon collection and stored in dark until used for analysis. An aliquot was taken for moisture determination in order to report the analytical result on the basis of dry sediment. Kjeldahl-nitrogen and organic carbon was run on the dry samples as an index of the organic content of the sediment.

Pheophytin standard solution. Pheophytin solution was prepared by the method of ZSCHEILE and COMER (1941).

Procedure. The wet sediment was placed

* Received Nov. 29, 1960. This work was done at Department of Chemistry Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo.

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in a porcelain mortar, and 10 milliliters of 90 per cent acetone was added. The sample was grinded well and the mixture transferred into 100 milliliter flask with stopper. The mortar was cleaned with a fresh portion of 5 milliliter of acetone and the wash solution was added to the flask.

The flask was kept overnight in a dark cold room. After extraction, the filtrate was transferred to 50 or 100 milliliter separatory funnel containing 10 milliliters of benzene. A few milliliters of acetone was used to rinse the flask and complete the transfer. The contents were mixed very vigorously for 1 to 2 minutes. After the layers were well separated, the acetone solution of lower layer was discarded and then benzene layer was washed twice with each 10 milliliter portions of distilled water. The benzene solution was drained into a 50 milliliter flask, and dried with anhydrous sodium sulphate.

The drying agent was removed by filtration through a 5A filter paper, and the filtrate drained into 20 milliliter volumetric flask. The flask, funnel, and drying agent were rinsed with small portion of benzene and the volume was adjusted to 20 milliliters. A portion of this solution was transferred to a 1 cm glass cell and the absorbance was determined in a Beckman type spectrophotometer. Generally only the spectras region from 600 to 700 millimicron was run. The major pigments have identical absorption maxima and the solution gives a fairly sharp maximum at about 665 millimicrons in benzene by our spectrometer, from which the pigments were calculated as pheophytin equivalence in micrograms per gram of dry sediment.

The procedure adopted represents a compromise between complete recovery and a reasonable time for analysis. Duplicate determinations generally agree to better than 5 per cent.

3. Results and Discussion

Location of deposits sampling is shown in Fig. 1. Surface sediment samples from basins of Kagoshima Bay have been found to range from 6 to 53 ppm of chlorophyll derivatives calculated as pheophytin equivalent.

Results from 13 different samples are presented in Table 1. The station 12 which shows minimum content of pigments (6 ppm), is located near the active volcano "Sakurajima", and with a depth of 65 m. The deposit

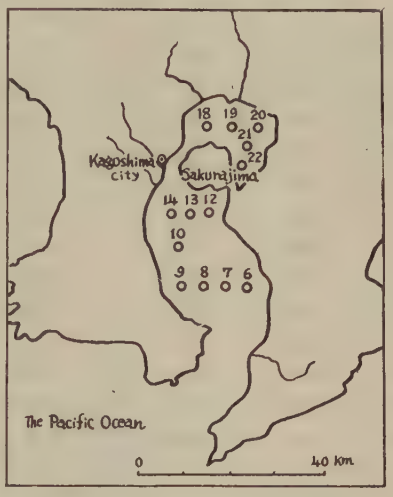

Fig. 1. Location of mud sampling of Kagoshima Bay.

is mainly composed of sand and the organic content is very poor. The other samples are almost composed of mud and mudy sand, and the content of organic matters is rather abundant, and the pigment content ranges from 21 to 53 ppm, and the mean value of pigment is 37.8 ppm. The pigment content of the St. 9 is 53 ppm, which is appreciably higher at the surface of any other basin sediment. But the organic and pigment content between sediments of outer part basin and inner part basin of Sakurajima is apparently different. At inner part basin, in order to runoff of surrounded areas, it is some what different from outer basins on the production, rate of sedimentation and decomposition in water column of organic matters.

The outer basin sediment ranges from 34 to 53 ppm, the median of 45 ppm of pigment content, and the inner basin sediment shows a range from 21 to 45 ppm, the median of 30 ppm of chlorophyll derivatives content. Organic carbon and total nitrogen are also grouping as described above.

These general trend in pigment content of the sediments can be understood qualitatively in terms of a balance between organic

Table 1. Organic content of surface muds from Kagoshima Bay.

Station	Depth in m.	Remarks	Org. *C* (%)	Total *N* (%)	*C*/*N*	Ignition loss (%)	Pheophytin ppm based on	
							dry sediment	org. matter
6	82	Mf	2.02	0.155	13.0	16.1	50	1440
7	192	Mf	2.08	0.241	8.6	21.2	34	950
8	200	Mf	2.03	0.240	8.5	20.0	51	1450
9	170	Mf	2.42	0.296	8.2	22.7	53	1280
10	107	Ms, G	1.50	0.090	16.0	13.1	39	1510
12	70	Sm	0.36	0.063	5.7	5.79	6	970
13	200	Mf	1.96	0.195	10	18.5	35	1040
14	110	Mf	1.28	0.129	10	15.0	42	1900
18	150	Mf	1.43	0.177	8.1	15.3	45	1820
19	135	M, G	0.70	0.109	6.4	10.0	34	2820
20	200	Mf	2.11	0.177	11	21.1	21	580
21	140	Mf	1.16	0.127	9.2	15.4	29	1450
22	135	M, G	1.18	0.106	11.1	10.7	21	1030

production, decomposition, and dilution by inorganic sediment.

Chlorophyll decomposition is perhaps best indicated by expressing the lipid content in terms of total organic matters rather than total sediments. The total organic matter in sediments is not easily determined but may be approximated from the organic carbon or total nitrogen content. According to TRASK, the total organic matter (marine humus) is about 1.74 times the organic carbon. Calculated from the total organic matter in this way, the parts of pheophytin equivalent per million parts of organic matter are included in Table 1. The abundance of pigment based on organic matter rather than total sediment should be independent of production and dilution by inorganic sediments, it is thus a measure of the relative rates of decomposition of chlorophyll derivatives and organic carbon.

The concentration of pigment in organic matter ranges from a maximum of 2820 ppm in station 19 sample to a minimum of 580 ppm in station 20 sample.

Some comparison can be made between the chlorophyll content of phytoplankton and the pheophytin content of organic matter in sediments.

From the available data (BRANDT and RABEN 1921, HARVEY 1934, RILEY 1938, GILLBRICHT 1952, ATKINS and JENKINS 1953) it appears that the organic matter suspended in the surface sea water (living cells and detritus on an ash free dry weight basis) contains 2–10% of green pigments estimated as chlorophyll; the median of 6%, or 60,000 ppm is a reasonable value to assume until better data become available. The difference in molecular weight between chlorophyll and pheophytin can be neglected in view of the other approximations which must be made.

Comparison of the pigment content with 60,000 ppm in phytoplankton indicates a preservation of 2.4% of the chlorophyll in station 19 and 0.97% in station 20 if carbon and pheophytin took similar behavior. The carbon loss is believed to be at least 90% and therefore the chlorophyll derivatives deposited in the surface sediments of these basins represent only 0.25% and 0.097%, respectively, of that produced by phytoplankton.

Table 2 lists the ranges and averages of pheophytin content for basin floor samples expressed as (1) parts per million parts of dry sediment and (2) parts per million parts of organic matter. The former values (1) represent the net result of production, decomposition, and dilution by inorganic matters, but the latter (2), being based only on composition of the organic matter, should be

Table 2. Range and averages for pheophytin, carbon, and nitrogen in sediment samples of Kagoshima Bay.

Sample Group	No. of Samples	Depth Range in m.	Org. *C* (%)	Total *N* (%)	*C*/*N*	Pheophytin ppm based on	
						dry sediment	org. matter
Outer basin	7	82-200	1.28-2.42 (1.89)*	0.090-0.296 (0.192)	8.2-16 (9.84)	35-53 (43.4)	950-1900 (1367)
Inner basin	5	135-200	0.70-2.11 (1.32)	0.106-0.177 (0.139)	6.4-11.1 (9.49)	21-45 (30.0)	580-2820 (1540)
Sand	1	70	0.36	0.063	5.7	6	970

* Mean value showed in round brackets.

independent of production and dilution except as these factors may have secondary effects on decomposition.

Therefore, comparison of the two sets of values in the different basins should give some idea of the importance of production and dilution as compared with decomposition in determining the pigment abundance in basin sediments.

In view of relation between carbon and pheophytin content, shows good agreement in Fig. 2. However depth relation did not

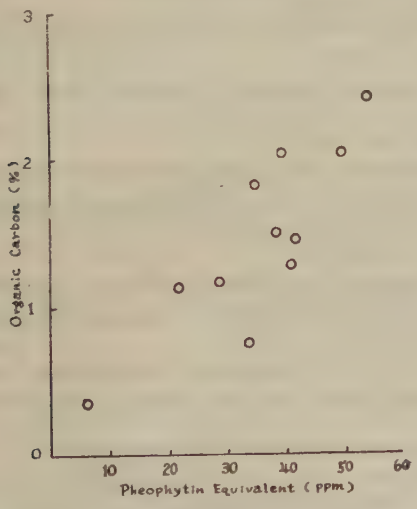

Fig. 2. Relation between organic carbon and pigment.

found for these samples.

Fig. 3 shows the absorption spectrum of typical acetone extracts from a few basin sediments. The absorption spectrum maxima at 667, 611 535, and 414 millimicrons are characteristics of phorbines or phorbides de-

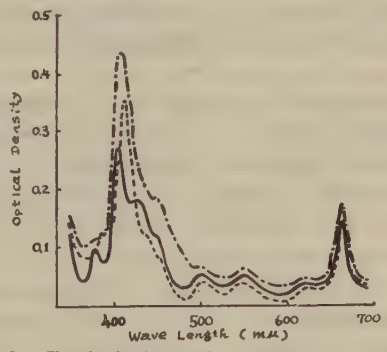

Fig. 3. Typical absorption spectra of sediment extract (90% acetone).
——; St. 9, - - -; St. 13, - · -; St. 19.

rived from chlorophyll *a* (Aronoff 1950). This correspondence is shown by comparison of maxima with the curve for pheophytin *a* which is included in Fig. 4.

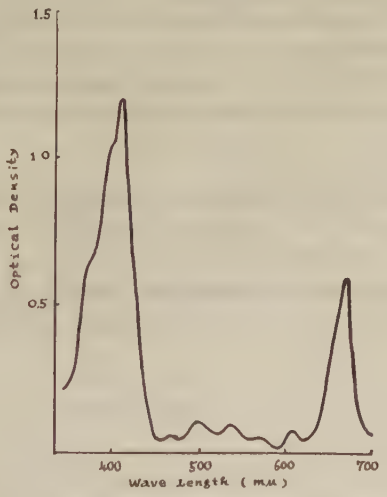

Fig. 4. Absorption spectrum of pheophytin *a* in acetone.

Much less is known about the mode of decomposition of chlorophyll derivatives under conditions in sea water and sediments. The biological decomposition of chlorophyll has been investigated from various standpoints, but the applicability of these studies to the marine environment is limited. In surface waters, enzymatic oxidation may occur in dead phytoplankton, but it is less probable in the sediments.

The results of this study may be generalized to conclude that most marine sedimentary environments around Japan contains sufficient content of chlorophyll derivatives to furnish the major porphyrins found in crude oils.

The content of pigment is comparable to that of the sediment of off California basin.

A more complete understanding of the effect of the sedimentary environment on chlorophyll preservation would be facilitated by data on sedimentation rates in this area. For a better understanding of the geochemical significance of porphyrins in the origin of petroleum, a careful investigation is needed to determine the exact chemical nature of the porphyrins in sediments.

4. Summaries

(1) Sediment samples of the basin floor of Kagoshima Bay contain substantial amounts of chlorophyll derivatives.

(2) According to the content of chlorophyll derivative based on organic matter, the ratio of decomposition of organic detritus settling through water column is estimated at least 95%.

The author wishes to express his appreciation to Dr. K. Noguchi, Professor of the Tokyo Metropolitan University for aid and encouragement through the course of this investigaiton, and he is indebted to Dr. M. Hoshino, Maritime Safety Agency, for collecting the samples.

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海洋に関する化学的研究 (第87報)

汀土のモリブデン含量について (2)*

山　本　善　一**

Chemical Studies on the Ocean-LXXXVII.

Molybdenum Content of the Shallow-water Deposits (2)

Yoshikazu YAMAMOTO

Abstract: In this paper, the analytical dada of 59 kinds of shallow-water deposits from the sea-coasts of Honshū (Japan) and Korea are given. Summarizing these data and those given in the previous paper, it is found that the molybdenum contents range trace to 3.6×10^{-4} percent in Japanese deposits and from trace to 3.0×10^{-4} percent in Korean ones, being in general higher in muds than in sands, and the molybdenum content is generally higher in the muds which are comparatively poor in SiO_2, Fe_2O_3, MgO and rich in S. Furthermore, the analytical data of the 24 kinds of deposits from various small islands having relatively simple geological structure and those of the samples of different depths collected at Kasaoka Bay, Okayama Prefecture and Oki, Shimane Prefecture are also given in this paper.

1. 緒　　言

前報[1]においては本州沿岸の汀土 81 種の Mo 含量を報告したが，今回は本州沿岸の汀土29種，朝鮮沿岸の汀土 30 種，計 59 種の汀土の Mo 含量を記すとともにこれに前報の結果を加え，本州，朝鮮全沿岸の試料の分析結果についての総括的考察を報告する。なお，汀土の Mo 含量と陸地の地質，水深との関係をしらべる目的で，地質的に比較的均一な島より採取した 24 種の汀土および水深をかえて採取した 12 種の汀土の分析を行なつたので，その結果をもあわせて報告する。

2. 実 験 方 法

モリブデンの定量方法は前報[1]の通りである。

3. 実験結果およびその考察

実験結果を第 1 表に示す。数値は吸着海水に由来する塩分を除外した乾燥試料に対するものである*。

Table 1. Molybdenum content of the shallow-water deposits.

Sample No.	Locality	Type of deposits	Mo content 10^{-4} %
83	Suna, Hasunuma-mura, Sanbu-gun, Chiba-ken	light brown sand	trace
84	Hamamachi, Anesaki, Anesaki-machi, Ichihara-gun, Chiba-ken	blackish gyay sand	0.5
85	Hon-machi, Funabashi-shi, Chiba-ken	light brackish brown sand	0.8
86	Kanazawa-machi, Isogo-ku, Yokohama-shi, Kanagawa-ken	grayish sand	0.9
87	Ōiso, Ōiso-machi, Naka-gun, Kanagawa-ken	blackish sand	0.8
88	Sakawa, Sakawa-machi, Ashigaranoshimo-gun, Kanagawa-ken	blackish sand	0.5

* 昭和 35 年 10 月 29 日受理

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* 吸着海水の補正は既報石橋，上田 Bull. Inst. Chem. Res. Kyoto Univ., **33**, 167 (1955) によつた。

Sample No.	Locality	Type of deposits	Mo content 10^{-4} %
89	Usami-mura, Tagata-gun, Shizuoka-ken	blackish brown sand	0.6
90	Tago, Tagonoura-mura, Fuji-gun, Shizuoka-ken	blackish gray sand	0.5
91	Chihama, Chihama-mura, Ogasa-gun, Shizuoka-ken	light blackish gray sand	0.4
92	Hamana, Arai-machi, Hamana-gun, Shizuoka-ken	light blackish gray sand	0.4
111	Namiita, Shishiori-mura, Motoyoshi-gun, Miyagi-ken	grayish sandy mud	0.7
93	Namiita, Shishiori-mura, Motoyoshi-gun, Miyagi-ken	grayish mud	3.1
94	Shizukawa-machi, Motoyoshi-gun, Miyagi-ken	grayish white sand	trace
95	Ōmagari, Yamoto-machi, Monou-gun, Miyagi-ken	light brown sand	1.6
96	Nakahama, Sakamoto, Sakamoto-mura, Watari-gun, Miyagi-ken	light yellowish gray sand	trace
97	Shin-machi, Ukedo, Ukedo-mura, Futaba-gun, Fukushima-ken	light brownish gray sand	0.5
98	Naka-machi, Yotsukura-machi, Iwaki-gun, Fukushima-ken	light yellowish gray sand	trace
99	Kawajiri, Toyoura-machi, Taga-gun, Ibaraki-ken	light brownish gray sand	0.6
100	Akashi, Namino-mura, Kashima-gun, Ibarakiken	light brownish gray sand	0.5
101	Yoshimi, Tajiri-mura, Sennan-gun, Ōsaka-fu	yellowish brown sand	0.1
110	Kamiya-machi, Kishiwada-shi, Ōsaka-fu	yellowish brown sand	0.7
102	Shiomi-machi, Izumiōtsu-shi, Ōsaka-fu	light yellowish brown sand	0.4
103	Hamazume-mura, Takeno-gun, Kyōto-fu	light brown sand	0.6
104	Iwagahana, Yōrō-mura, Yoza-gun, Kyōto-fu	light brown sand	trace
109	Shimasaki, Miyazu-machi, Yoza-gun, Kyōto-fu	light brown sand	trace
105	Higashikanzaki, Kanzaki-mura, Kasa-gun, Kyōto-fu	light brownish gray sand	0.8
106	Wakamiya, Takahama-machi, Ōi-gun, Fukui-ken	greenish black sand	0.4
107	Shirahige, Obama-machi, Onyū-gun, Fukui-ken	grayish brown sand	0.5
108	Ishishinbo, Natsume-mura, Sakai-gun, Fukui-ken	brown sand	1.5
K 1	Puna, Yongchon-kun, Pyongan-pukto	dark brown mud	n.d.
K 2	Osong-tong, Taesan-myon, Sonchon-kun, Pyongan-pukto	〃	0.9
K 3	Hampal-ri, Hanchon-myon, Pyongwon-kun, Pyongan-namdo	〃	1.1
K 4	Okyangki-ri, Chinnampopu, Pyongan-namdo	〃	1.3
K 5	Yonghoto-ri, Tongnam-myon, Ongjin-kun, Hwanghae-do	〃	1.3
K 6	Chinjong-ri, Sonwon-myon, Kanghawa-kun, Kyonggi-do	〃	trace
K 7	Tongjoung-ri, Sokumun-myon, Tangjin-kun, Chungchong-namdo	〃	0.7
K 8	Sopinchon, Kunsanpu, Cholla-pukto	〃	1.2
K 9	Namchang-ri, Pukpyong-myon, Haenam-kun, Cholla-namdo	〃	1.0
K 10	Mayang-ri, Taeku-myon, Kangjin-kun, Cholla-namdo	〃	0.6
K 11	Haean, Kuhangshine, Yosu-ub, Yosu-kun, Cholla-namdo	〃	1.9
K 12_1	Royang-ri, Kumnan-myon, Hadong-kun, Kyongsang-namdo	dark brown sandy mud	0.7
K 12_2	Koyang-ri, Kumnan-myon, Hadong-kun, Kyongsang-namdo	dark brown mud	0.7
K 13	Sonjin-ri, Yongkyoun, Sachon-kun, Kyongsang-namdo	dark brown sandy mud	0.6
K 14	Tupu-ri, Samsan-myon, Kosong-kun, Kyongsang-namdo	dark brown mud	1.4

Sample No.	Locality	Type of deposits	Mo content 10^{-4} %
K 15	Shinjon-ri, Sanyang-myon, Tongyon-kun, Kyongsang-namdo	dark brown sandy mud	1.1
K 16	Kyonghwa-tong, Chinhae-ub, Changwon-kun, Kyongsang-namdo	brown mud	3.0
K 17	Chedok-ri, Ungchon-myon, Changwon-kun, Kyongsang-namdo	dark brown mud	1.0
K 18	Bangou-ri, Tong-myon, Ulsan-kun, Kyongsang-namdo	yellow clay	1.9
K 19_1	Pohang-tong, Pohang-ub, Yongil-kun, Kyongsang-pukto	dark brown mud	1.3
K 19_2	Pohang-tong, Pohang-ub, Yongil-kun, Kyongsang-pukto	light yellowish brown sand	trace
K 20	Imwon-ri, Wondok-myon, Samchok-kun, Kangwon-do	〃	0.4
K 21	Chumun-ri, Chumunjin-myon, Kangnung-kun, Kangwon-do	yellowish white sand	trace
K 22	Haean-tong, Wonsanpu, Hamgyong-namdo	light yellowish brown sand	0.4
K 23	Hengchon, Songjin-ub, Songjin-kun, Hamgyong-pukto	light brown sand	1.5
K 24	Songshin-tong, Ouyang-myon, Kyongsong-kun, Hamgyong-pukto	〃	0.4
K 25	Tokyoun-tong, Ochon-myon, Kyongsong-kun, Hamgyong-pukto	grayish white sand	2.6
K 26_1	Bipa-tong, Songpyong-tong, Unggi-ub, Kyonghung-kun, Hamgyong-pukto	〃	0.5
K 26_2	Ungsang,tong, Unggi-ub, Kyonghung-kun, Hamgyong-pukto	light yellowish brown sand	trace
K 26_3	Unggi-tong, Unggi-ub, Kyonghung-kun, Hamgyong-pukto	grayish whitd sand	trace
K 27	Sosura-tong, Roso-myon, Kyonghung-kun, Hamgyong-pukto	〃	0.4

1) 各地沿岸の汀土の Mo 含量

第1表より各地沿岸の Mo 含量をみるに，千葉県，神奈川県，静岡県沿岸の試料についてはいずれも Mo が少く，殊に千葉県蓮沼村沿岸の試料83は痕跡となつている。宮城県，福島県，茨城県沿岸の試料では，宮城県鹿折村沿岸の泥土の試料93に Mo が著しく多く，ついで矢本町沿岸の淡褐色の砂の試料 95 に比較的多いのが認められる。一方，志津川町沿岸の試料 94，坂元村沿岸の試料96および福島県四倉町沿岸の試料 98 は灰白色ないし黄白色の砂であつて，その Mo 含量は痕跡となつている。大阪府，京都府，福井県沿岸の汀土については，福井県棗村沿岸の茶褐色の砂の試料108 に Mo が比較的多いが，他は概して少く，特に京都府養老村沿岸の試料104，宮津湾の試料109は痕跡にすぎない。

朝鮮西沿岸の試料（K 1～K 8）および海峡側沿岸の試料（K9～K18）については，平安南道鎮南浦府沿岸の試料 K4，黄海道東南面沿岸の試料 K 5，全羅南道麗水邑沿岸の試料 K 11，慶尚南道三山面沿岸の試料 K14，慶尚南道東面沿岸の試料 K 18 に Mo が比較的多く，特に慶尚南道南邑沿岸の試料 K 16 に著しく多い。これらのものは試料 K 18 が黄色の粘土であるほかいずれも暗褐色の泥土である。東沿岸の試料（K19_1～K27）については，これらはほとんど砂であつて，咸鏡北道城津邑沿岸の試料 K 23，咸鏡北道梧村面沿岸の試料 K25 に Mo が比較的多いが，他はいずれも痕跡ないしそれに近い値を示している。

2) 本州，朝鮮全沿岸の汀土の Mo 含量に関する総括的考察

前報[1]の結果と本報のそれとを一括し，本州，朝鮮の全試料，砂，泥土につきそれぞれ Mo 含量の最大値，最小値，平均値を求めると第2表のごとくなる。本州沿岸の各平均値を朝鮮沿岸のそれと比較するに，全試料および砂の平均値は本州が朝鮮より僅かに低く，泥土の平均値においては本州が朝鮮より僅かに高くなつている。また砂と泥

Table 2, Summary of Table 1.

Number of samples		Mo content (10^{-4}%)		
		Maximum	Minimum	Average
Total samples fron Japan	110	3.6	trace	0.7
Sands	80	2.2	〃	0.5
Muds*	30	3.6	〃	1.3
Total Samples from Korea	30	3.0	〃	0.9
Sands	11	2.6	〃	0.6
Muds*	19	3.0	〃	1.1

* Sandy muds and clay are also included.

土の平均値においては，本州，朝鮮いずれにおいても泥土が砂より高い値を示している。前報[1]ならびに本報の第1表より明らかなように泥土においては痕跡の試料が少く，砂に比してMo含量の高いものが多い。これは浅海の泥土が還元力に富み，Moを硫化物として沈澱せしめる傾向のあること[2]および吸着などの種々の要因によつて濃縮されるものと考えられる。

さらに本州および朝鮮沿岸の泥土のMo含量を深海底土のそれと比較するに，小穴氏[3]による深海底土12種のMoの平均値 12.3×10^{-4} % ならびに黒田氏[4]による6種の平均値 3.1×10^{-4} % に比べて汀土の Mo 含量はかなり少い。既に浜口氏[5]は海底土のラジウム含量に関して，遠洋深海においては充分酸化性環境にあるため，ラジウムなどが Fe, Mn のコロイド性酸化物に伴われつつ沈澱して濃縮せられるのに対し，浅海においては，底部に有機物を保持して還元的作用を呈し，Fe, Mn を溶存し得るのでラジウムの濃縮は起らぬと報告しておられる。浅海底土のMoについてもこれと同様な傾向が存在するのではないかと思われる。

つぎにMo含量と他の含有元素との関係については，これらの間に明瞭な関連性は認められないようである。とくに砂の試料にこの傾向が著しいのであつて，既報[6]において SiO_2 が多く，Fe_2O_3, CaO, MgO などのきわめて少い砂と，SiO_2 がきわめて少く，Fe_2O_3, CaO, MgO などのきわめて多いものでは，Cu, Zn, Pb などの含量にかなりの相違がみられたのであるが，Mo 含量についてはあまりその差が認められない。一方，泥土については，SiO_2 が少なく Fe_2O_3, MgO などの多い試料，とくにSの多い試料にMoが多くなつているようであるが，例外もあり一般的な傾向とはいい難い。

3) 汀土のMo含量と地質との関係

つぎに汀土のMo含量と試料採取地附近の陸地の地質との関係については，上記の本州，朝鮮沿岸の試料は陸水，沿岸流などで遠隔の地域の影響を受けることも予想され，そのMo含量を試料採取地附近の地質にのみ関連せしめることは困難である。よつて他の地帯の影響をうけぬよう島嶼*を対象として選び，その周辺よりそれぞれ2～5種の汀土を採取し，それらの混成試料の化学分析を行ない，汀土のMo含量と地質との関係をしらべた。実験結果を第3表に示す。数値は吸着海水に由来する塩分を除外した乾燥試料に対するものである。第3表より明らかなように，広島より田島までの主として酸性の火成岩より成る地帯の汀土においては，それらのMo含量は痕跡～3.3×10^{-4}%であつて，横島の汀土にMo含量が飛びぬけて高いことが認められる。平郡島および梶島は主として基性の火成岩より成るが，それらの Mo 含量については，上記のものと著しい差異は認め難い。笠戸島より沼島に至る変成岩類のMo含量は上記の火成岩類のものとほぼ類似した値を示しており，笠戸島の試料にやや多いのが認められる。ついで志々島より日間賀島に至る堆積岩類で

* 2～3 の岬を含む。

Table 3. Molybdenum content of the shallow-water deposits collected from small islands.*

Locality	Geology**	Type of deposits	Composite of	Mo content 10^{-4}%	SiO_2 %	Fe_2O_3 %	Al_2O_3 %	MnO %	CaO %	MgO %	CO_2 %
Hiroshima, Kagawa-ken	Granites	grayish white sand	5 deposits	trace	82.92	0.56	9.23	trace	0.74	0.33	—
Nakashima, Ehime-ken	〃	light brown sand	5 〃	〃	79.28	1.26	11.01	0.01	1.09	0.34	—
Ogishima, Kagawa-ken	〃 (Sanukite)	〃	5 〃	〃	77.49	1.97	12.16	0.03	2.23	0.24	—
Momoshima, Hiroshima-ken	〃	〃	4 〃	0.4	75.81	2.34	12.21	0.04	1.69	0.40	—
Yokoshima, Hiroshima-ken	〃	〃	5 〃	3.5	76.21	2.49	14.77	0.03	1.32	0.25	—
Okinoshima, Kōchi-ken	〃	grayish brown sand	5 〃	0.4	73.96	3.08	10.40	0.04	3.76	0.46	2.33
Kogoshima, Ehime-ken	〃	broun sand	3 〃	trace	70.62	4.28	12.98	0.11	2.85	1.14	1.66
Kōnoshima, Okayama-ken	Quartz-porphyry	light brown sand	5 〃	〃	79.24	1.56	9.74	0.02	2.57	0.56	1.28
Tashima, Hiroshima-ken	〃 (Granites, Ryōke metamorphics)	greenish sandy mud	5 〃	0.5	75.87	2.02	11.52	0.03	0.90	0.49	—
Hegunshima, Yamaguchi-ken	Pyroxene-andesite	grayish brown sand	2 〃	0.9	71.20	2.98	13.49	0.04	2.92	1.87	—
Kajishima, Ehime-ken	Norite	light blackish gray sand	5 〃	0.5	52.64	8.25	20.06	0.18	9.69	4.58	0.52
Kasatoshima, Yamaguchi-ken	Ryōke metamorphics (Granites)	grayish brown sandy mud	4 〃	1.2	79.36	3.05	6.82	0.11	2.82	1.12	1.58
Ōtsushima, Yamaguchi-ken	Sangun metamorphics (Granites)	blackish green sand	2 〃	trace	47.48	6.14	12.31	0.12	15.95	2.74	8.28
Takashima, Ōita-ken	Sanbagawa metamorphics	grayish blue sand	5 〃	0.5	70.02	2.87	9.51	0.06	7.05	1.86	4.01
Nushima, Hyōgo-ken	Greenshist, Black phyllite	grayish white sand	5 〃	0.8	74.26	2.16	7.07	0.06	5.62	0.74	5.86
Shishishima, Kagawa-ken	Upper paleozoic formations	light brown sand	5 〃	0.8	87.54	1.00	5.77	0.04	1.19	0.21	—
Mutsukishima, Ehime-ken	Upper Paleozoic formatiohs (Granites)	yellowish brown sand	2 〃	trace	79.25	1.02	10.05	0.01	2.13	0.52	—
Ōnyūshima, Ōita-ken	Mesozoic formation	brown sand	4 〃	0.7	76.42	2.99	10.95	0.03	1.80	0.26	0.50
Shimoniizu-mura, Ōia-ken	〃	〃	5 〃	1.0	70.67	5.21	13.37	0.08	0.76	1.10	—
Sugari, Owashi-shi, Mie-ken	〃	blackish gray sand	4 〃	0.7	72.20	3.38	11.27	0.04	3.45	0.65	1.20
Tobishima, Yamagata-ken	Tertiary formation	〃	4 〃	0.8	57.69	3.69	14.82	0.05	8.56	2.20	5.14
Higashitonda-mura, Waka-yama-ken	〃	light blackish gray sand	4 〃	1.7	56.25	2.76	7.15	0.01	15.27	1.25	11.28
Himagashima, Aichi-ken	〃	light grayish brown sand	5 〃	1.2	77.54	1.79	8.77	0.01	3.83	0.51	2.18

* Three capes are also included.

** Only the predominant rocks and formations are shown. The parentheses are for the rocks which distribute in the land areas relatively for from the location sampled.

Table 4. Molybdenum content and the geology (Summary of Table 3).

Geology	Number of samples	Mo content (10^{-4}%)	
		Range	Average
Igneous rocks			
Acidic rocks	9	trace～3.5	0.5
Basic rocks	2	0.5 ～0.9	0.7
Metamorphic rocks			
Gneisses	1	——	1.2
Crystalline schists	3	trace～0.8	0.4
Sedimentary rocks			
Upper paleozoic formations	2	trace～0.8	0.4
Mesozoic formations	3	0.7 ～1.0	0.8
Tertiary formations	3	0.8 ～1.7	1.2

Table 5. Molybcenum content of the deposits of various depths.

Kassaoka Bay, Okayama Prefecture

Depth (m)	Number of samples	Type of deposits	Mo content (10^{-4}%)
1.7～ 3.4	3	mud	2.0
6.7	2	〃	0.6
9.2～13.1	2	〃	1.3
15.8～17.3	3	〃	0.8
19.1～21.9	3	〃	1.6
39	1	〃	1.5

Oki, Shimane Prefecture

Depth (m)	Number of samples	Type of deposits	Mo content (10^{-4}%)
9.3	1	mud	1.5
11.8	1	〃	1.3
23	1	〃	0.9
27	1	〃	1.2
36	1	〃	0.6
41	1	〃	1.2

は，第三系の地帯の汀土にやや多い。また時代未詳の中生界は大部分が頁岩よりなり，比較的深海で沈積したものと考えられているのでMo含量の比較的高いことを予想したのであるが，結果はこれに反しあまり著しい値を示していない。以上の結果を総括すると第4表の如くなる。

4) 汀土のMo含量と水深との関係

汀土のMo含量と水深との関係をみるため，岡山県笠岡湾および島根県隠岐浦郷より深度をかえて12種の試料を採取し，それらの分析を行なつた。分析結果を第5表に示す。すなわち，笠岡湾の試料のMo含量は $0.8～2.0\times10^{-4}$% であり，隠岐のそれは $0.6～1.5\times10^{-4}$% であつて，いずれの場合においてもこの程度の水深の変化ではほとんどMo含量に大差が認められない。汀土のMo含量と水深との関係については，今後さらに多数の試料を採取して検討する必要があると思われる。

本研究を行うに際し，御懇篤な御指導を賜わつた京都大学石橋雅義教授ならびに金沢大学上田俊三教授に深甚の謝意を表する。

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On the Variation of Silicate Content in Sea Water during its Storage*

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Abstract: As the first step in the investigation of silicate in sea water, dissolution of silicate from various kinds of containers and from organic remains during the storage was studied.

The amount of dissolution of silicate from glass bottles during its storage was fairly large, which was more than 10^5 μg-atoms/L on an average about a month later from the collection of samples, though the effect was different with different nature of glass materials of each bottle.

Rapid dissolution of silicate from plankton diatoms was also found when sea water contained plankton diatoms of more than 10^5 in cell numbers per liter.

By these reasons it is recommended that silicate determination in oceanographic research should be done on board soon after sampling. If this is impossible, sea water should be filtered off and stored in paraffine coated bottles.

1. Introduction

A large number of studies have been done about the silicon in sea water, i.e. regarding its chemical form of the element determined colorimetrically by the method of DIENERT and WANDENBULCKE, salt error in the determination of silicate in sea water, variation of silicate content during the storage of samples, and procedures for analyses. Results obtained from these examinations, however, are sometimes not consistent.

Many workers have pointed out that the silicate content in samples of sea water changes considerably during its storage. This change is attributed to the effect of dissolution of silicon from glass bottles, disintegration of microorganisms as well as organic matter suspended in sea water, and transition among the ionic, molecular or colloidal state of silicon.

The present authors have attempted to clarify a change of silicate in sea water during its storage in regard to each factor which gives rise to the change. Results of some experiments are preliminarily reported in this paper. The authors have also attempted to find out a possibility of correction of data obtained for samples which are kept in bottles for more than a month after their collections, although this attempt has not been successful.

* Received Nov. 2, 1960.

** Nagasaki Marine Observatory.

2. On the Variation of silicate content in sea water stored in sampling bottles

We have colorimetrically determined on board the silicate content in sea water of some thousands of samples collected in the seas west of Japan during a number of voyages of R.M.S. "Shumpū-maru" and R.S.S. "Umikaze-maru" since 1954. All these samples have been determined again with respect to the silicate in the laboratory in order to examine the variation in silicate content about one month after sampling. In most bottles silicate increased more or less, and the additional value was 10.4 μg-atoms/L on an average, which was higher than that in the surface water in the Kuroshio region. It should be noticed that the additional values of individual bottles were considerably different, ranging 0 to 60 μg-atoms/L. The silicate contents and their variations during the storage are shown in Tables 1 and 2, for the samples collected at the representative points of the Kuroshio and the Yellow Sea regions.

The horizontal distribution of silicate in the seas west of Japan is drawn using two series of data in Fig. 1, in which the solid lines were obtained by plotting the values

Tables 1 and 2. Silicate contents of the samples collected in Kuroshio and Yellow Sea regions and their variations during the storage (μg-atoms/L).

Depth	A	B	C
0m	2.5	11.7	9.2
10	2.5	10.8	8.3
25	2.5	6.7	4.2
50	2.5	6.7	4.2
75	2.5	10.0	7.5
100	2.5	10.0	7.5
125	3.3	31.7	28.4
150	3.3	9.2	5.9
200	3.3	10.0	6.7
250	5.0	13.3	8.3
300	10.0	21.7	11.7
400	20.0	31.7	11.7
500	40.0	60.0	20.0
750	75.0	83.3	8.3
1000	75.0	90.0	15.0

Depth	A	B	C
0m	5.0	20.0	15.0
10	3.3	12.5	9.2
25	3.3	13.3	10.0
50	3.3	25.0	31.7
75	5.0	10.0	5.0

Column A: determination soon after their collections
〃 B: determination about a month later
〃 C: additional values during their storage (B minus A)

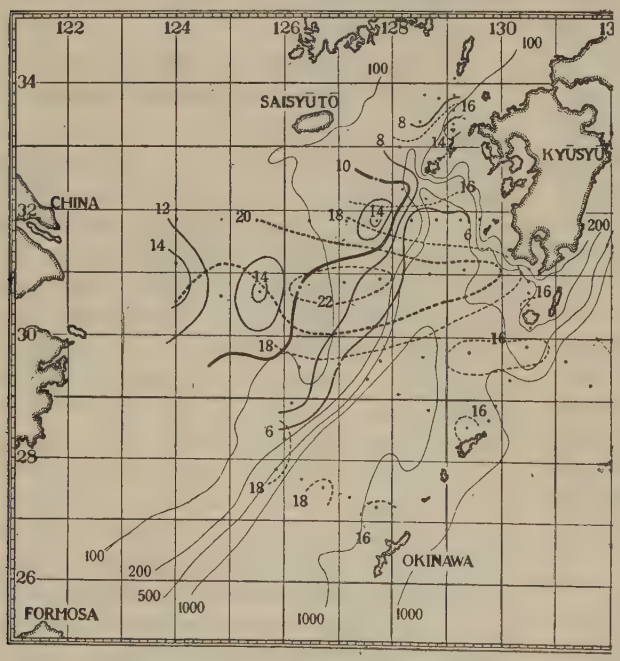

Fig. 1. Horizontal distribution of silicate in summer, 1954 (μg-atoms/L).

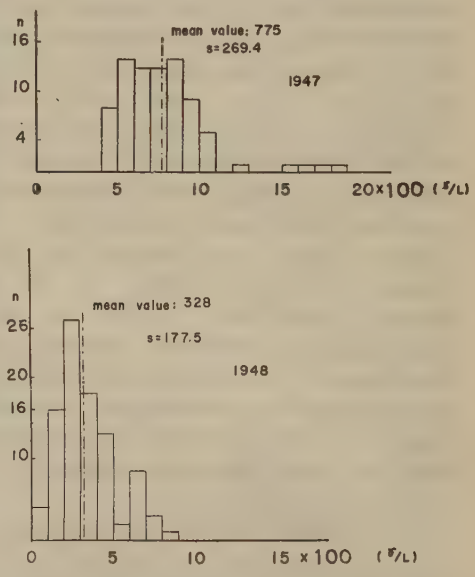

Fig. 2. Statistical data obtained from the daily determination of silicate at Misaki Channel (γ/L).

of analyses made on board immediately after the sampling was done, while the dotted lines were those obtained from the analyses made at the laboratory about a month later.

One of the present authors investigated the annual variation of silicate for three years from 1947 to 1949, as well as water temperature, dissolved oxygen, chlorinity, nitrite, and phosphate at the Misaki Channel situated on the Pacific coast of Honshū. Chemical constituents were determined once for one to seven days in the first year, and

every day in later two years. In the first year, the curve of annual variation of silicate was not smooth, and its content was larger in general than that in the latter two years. The annual variation of silicate in the latter two years corresponds closely to that of chlorinity in an inverse correlation. Statistical results obtained from these data are shown in Fig. 2.

With the experiences mentioned above it may be said that the variation of silicate in containers during its storage should not be neglected in oceanographic research of sea conditions.

3. Experiments and Discussion

1) *Estimation of the amount of silicate dissolved from containers*

In these experiments, sea water and distilled water were used for the examination and

Table 3. Variation of silicate contents of sea water samples (μg-atoms/L).

	0	2	6	10	14	24 days
I	$5.0^{*}\pm0^{**}$	5.4±0.2	$6.6^{+1.2}_{-1.1}$	$7.4^{+2.0}_{-1.4}$	$8.6^{+1.4}_{-0.8}$	$9.5^{+1.7}_{-0.9}$
II	5.0±0	5.0±0	5.1±0.1	$5.0^{+0.1}_{-0.0}$	$5.1^{+0.1}_{-0.0}$	$5.2^{+0.0}_{-0.1}$
III	4.9±0.1		$4.8^{+0.2}_{-0.0}$	4.9±0.1	$4.8^{+0.2}_{-0.1}$	$4.9^{+0.3}_{-0.2}$
IV	5.0±0		5.0±0	5.0±0	5.1±0	5.0±0

*: mean value
**: range of variation from the mean value
I: sampling bottles usually used
II: paraffine coated bottles on their internal walls
III: organisms were removed by filtration (paraffine coated)
IV: organisms were removed centrifugally (paraffine coated)

Table 4. Variation of silicate contents of sea water samples stored in various vessels (μg-atoms/L).

	0	1	4	10	20	30 days
A	$2.5^{*}\pm0^{**}$	4.0±0	5.0±0	$5.1^{+1.2}_{-1.1}$	$5.7^{+1.8}_{-0.7}$	$8.7^{+1.3}_{-1.2}$
B	2.5±0	2.5±0	2.5±0	$2.6^{+0.4}_{-0.1}$	$2.9^{+0.4}_{-0.2}$	$3.6^{+0.9}_{-0.6}$
C	2.5±0	3.0±0	$3.6^{+0.4}_{-0.1}$	$5.0^{+1.0}_{-0.3}$	$8.2^{+1.8}_{-2.2}$	10.0±0
D	2.5	3.0	3.8	7.5	14.2	18.3
E	2.5	3.0	3.0	5.0	4.2	4.5
F	2.5	3.0	3.0	6.0	7.5	10.8
G	2.5	3.3	3.3	4.0	4.2	4.5

*: mean value
**: range of variation from the mean value
Column A: sampling bottles usually used
〃 B: paraffine coated bottles on their internal walls
〃 C: sampling bottles designated by Central Meteorological Agency
〃 D: bottles for soft drinks made of crude glass
〃 E: beer bottles
〃 F: bottle of sake
〃 G: flasks made of hard glass

bottles made of various kinds of glass materials were employed as containers. In order to examine the dissolution from the inner walls of bottles, the organisms and their remains must be removed by filtering with filter papers (SS No. 5) or settling centrifugally before water samples are transferred into the bottles. The results are shown in Tables 3, 4 and Figs. 3–6.

Little differences in the variation of silicate content were found between the samples from which organisms were removed and those not removed. The most remarkable dissolution was found in samples kept in bottles made of crude glass which are commercially used for soft drinks. Considerable dissolution was also found in the case of A, C and F groups of bottles shown in Table 4, while no dissolution was found in bottles coated with paraffine on their internal walls[2], and in polyethylene vessels. A slight increase was seen in the case of bottles used for beer and of flasks made of hard glass. When these experiments were repeated a few times under the same conditions, almost the same results were obtained.

The mixed samples, consisting of sea water and distilled water, or sea water and

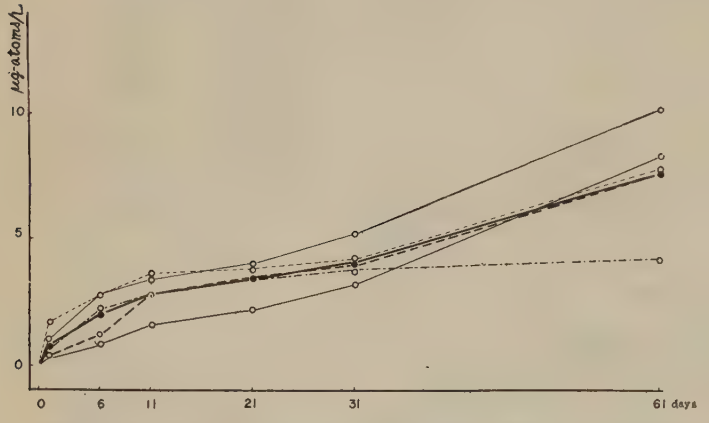

Fig. 3. Variation of silicate contents of distilled water samples stored in the same kinds of glass bottles (μg-atoms/L).
●: mean value

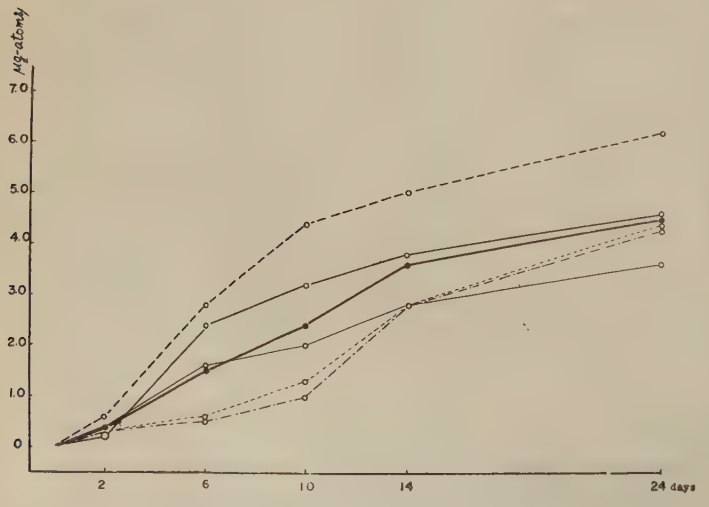

Fig. 4. Variation of silicate contents of sea water samples stored in the same kinds of glass bottles (μg-atoms/L).
●: mean value

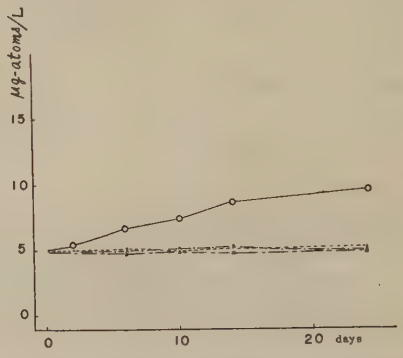

Fig. 5. Variation of silicate contents in sea water samples.
○: sampling bottles usually used
●: paraffine coated bottles on their internal walls
×: organisms were removed by filtration
□: organisms were removed centrifugally

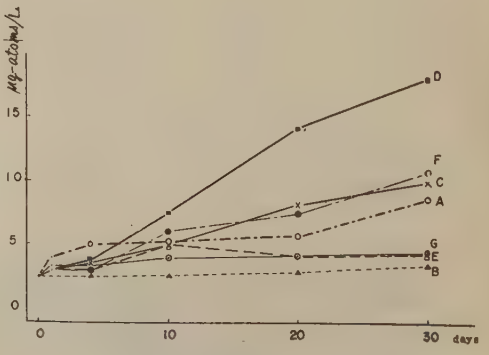

Fig. 6. Variation of silicate contents in sea water samples stored in various vessels (Table 4).

Table 5-1. Variation of silicate contents of the mixed samples (μg-atoms/L).

	Mixing ratio		0	1	8	22	58 days
Sea water		A	19.2	27.0	30.0	26.0	32.5
S. W.	3	A	16.7	22.5	23.3	22.5	26.7
		B	14.4	40.4	22.5	19.5	24.3
D. W.	1	C	+2.3	+2.1	+0.8	+3.0	+2.4
S. W.	2	A	9.2	19.2	19.2	19.2	21.7
		B	9.6	13.6	15.0	13.0	16.2
D. W.	2	C	−0.4	+5.6	+3.7	+6.2	+5.5
S. W.	1	A	—	10.8	10.0	11.7	11.7
		B	4.8	6.8	7.5	6.5	8.1
D. W.	3	C		+4.0	+2.5	+5.2	+3.6
Distilled water		A	0	0	0	0	0

Column A: measured
" B: calculated from the mixing ratio
" C: A minus B

Table 5-2. Variation of silicate contents of the mixed samples (μg/atoms/L).

	Mixing ratio		0	1	8	22	58 days
Sea water		A	19.2	26.0	30.0	26.0	32.5
S. W.	3	A	47.5	45.0	50.0	50.0	47.5
		B	45.7	49.5	53.8	54.5	54.4
L. W.	1	C	+1.8	−4.5	−3.8	−4.5	−6.9
S. W.	2	A	75.0	66.7	65.0	80.0	75.0
		B	72.1	73.0	77.5	83.0	76.3
L. W.	2	C	+2.9	−6.3	−12.5	−3.0	−1.3
S. W.	1	A	95.0	86.7	90.0	100.0	90.0
		B	98.6	96.5	101.3	116.5	98.1
L. W.	3	C	−3.6	−9.8	−11.3	−16.5	−8.1
Land water		A	125.0	120.0	125.0	140.0	120.0

Column A: measured
" B: calculated from the mixing ratio
" C: A minus B

land water were tested. In the latter case, the value was slightly smaller than the calculated value (Tables 5–1, 5–2)[5].

2) *Dissolution of silicate from the plankton diatoms and their remains*

Nutrient substances dissolved in sea water are taken up by organisms for their growth and multiplication. These substances return to a solution by disintegration of the organisms. Silicon is one of the essential elements for marine diatoms. As mentioned before, the influence of organisms and their remains on the silicate content in sea water should not be overlooked, therefore some experiments on the dissolution of silicate from the remains of diatoms were done. Samples of plankton used in these experiments were collected by means of surface hauling with KITAHARA's net. To prepare samples with various concentrations, plankton were diluted with surface water which stood still for a while, and were determined of its silicate content previously. In colorimetry, samples were filtered to remove planktonic remains

Table 6. Dissolution of silicate from the plankton diatoms (μg-atoms/L).

	0	1	5	11	21 days
I-1	2.7	17.5	17.5	17.5	37.5
I-2	2.7	10.0	11.7	10.0	14.2
I-3	2.7	7.5	7.5	6.3	7.5
I-4	2.7	4.2	5.0	5.0	5.0
I-5	2.7	3.8	3.8	4.7	4.2
II-1	2.7	17.5	19.2	20.0	
II-2	2.7	10.8	11.7	13.3	
II-3	2.7	8.3	8.3	8.3	
II-4	2.7	4:0	4.3	5.0	
II-5	2.7	4.0	4.0	4.2	
III-1	2.7	17.5	19.2	20.0	
III-2	2.7	10.8	10.8	10.0	
III-3	2.7	7.5	7.5	7.5	
III-4	2.7	3.7	4.0	4.2	
III-5	2.7	3.7	3.7	4.2	

I : natural sea water

II : chloroform was added with concentration of 5%

III : chloroform and toluene mixture was added with concentration of 5%

Table 7. Composition of plankton diatoms contained in samples (%).

	Exp. I	Exp. II	Exp. III
Bacteriastrum varians	0	0	5.6
Chaetoceros affinis var. willei	5.0	0	0
Chaetoceros at. v. skeleton	0	4.0	0
C. curvisetus	19.2	0	10.5
C. decipiens	15.4	0.8	2.8
C. densus	0	0	4.0
C. distans	3.9	0	0
C. messanensis	16.9	0	0
Coscinodiscus spp.	2.7	9.5	3.7
Ditylum brightwellii	0	0.9	0
Eucampia zoodiacus	0	0	3.4
Lauderia borealis	12.7	7.5	7.9
Nitzschia seriata	5.0	10.4	0
Rhizosolenia imbricata	0	2.3	0
Skeletonema costatum	0	15.6	0
Stephanopyxis palmeriana	0	1.1	0
Thalasionema nitzochioides	3.9	15.6	0
Thalassiosira subtilis	0	28.0	43.1
Thalassiothrix longissima	5.0	0	0
T. frauenfeldii	10.3	1.2	4.5
other phytoplankton		3.9	14.5
Total	100.0	100.0	100.0

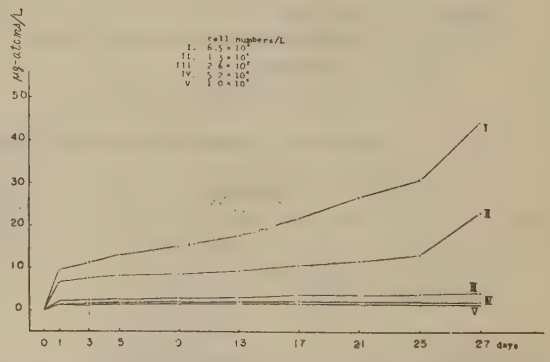

Fig. 7. Dissolution of silicate from the plankton diatoms (μg-atoms/L) (Exp. 1 in Table 6).

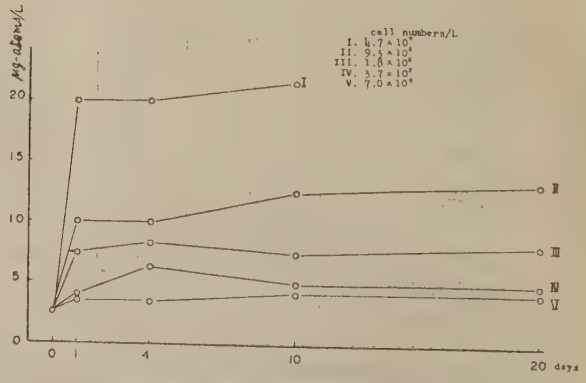

Fig. 8. Dissolution of silicate from the plankton diatoms (μg-atoms/L) (Exp. 2 in Table 6).

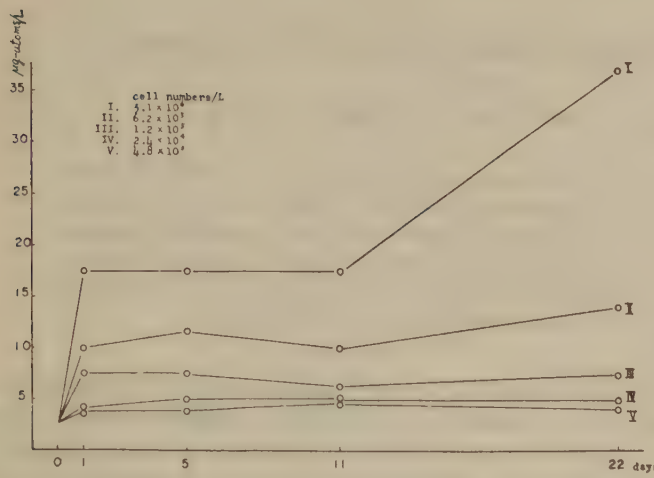

Fig. 9. Dissolution of silicate from the plankton diatoms (μg-atoms/L) (Exp. 3 in Table 6).

prior to the addition of reagents. The number of cells and species of plankton communities were determined microscopically (Table 7).

When a sample water contained plankton diatoms more than 10^5 of cells per liter, a remarkable increase of silicate was found. Especially at the beginning of the experiment, a rapid increase was observed. In some areas the number of plankton often exceeds the above quantity, especially such as in mixing regions of warm and cold water masses, in neritic regions or in bays. In such an area, analysis should be made immediately after sampling. To examine the effects of some reagents to prevent samples from decay, chloroform and chloroform-toluene mixture were added up to 5% in concentration, but those were not effective to control the change in silicate content.

Acknowledgements

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Carbon Dioxide Exchange between Air and Sea Water-I*

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Abstract: The equation $dq/dt=K(P-p)$ was assumed, where dq/dt is the exchange rate, P and p are the partial pressure of CO_2 in sea water and air, respectively. The apparatus for estimation of K value was described. The value of K was found to increase with increase in the flow rate with a little difference in the rate of increase between two cases of absorption and escape of CO_2 on and from the sea water. There was a sign that K value increased when the partial pressure of CO_2 in the sea water approached that of the air.

One of the most fascinating topics in modern geochemistry is the role of the ocean in regulating carbon dioxide in the atmosphere. Then many approaches have been made by investigators from various angles. Thus some investigators are determining and comparing the carbon dioxide contents in the atmosphere with those in the sea over extended areas of the world oceans, while others are concentrating their efforts to determine the distribution of carbon-14 in various terrestrial and marine materials.

The present study was initiated to make clear the magnitude of carbon dioxide exchange at actual interface between air and sea water as well as the conditions and processes which affect the rate of that exchange. Some of the results so far obtained will be given.

1. Expression of Exchange Rate of Carbon Dioxide between Air and Sea Water

Both absorption and escape of carbon dioxide by and from the sea water are tentatively assumed to be given approximately by the following equation:

$$\frac{dq}{dt}=K(P-p)\,. \qquad (1)$$

Here, P is the partial pressure of carbon dioxide in the sea water used and p is the corresponding pressure in the air expressed in the term ppm. And dq is the amount of carbon dioxide which escapes or is absorbed (mole/cm²) during the time dt (sec). Consequently K is the amount of carbon dioxide exchange (mole/cm² sec) on the condition that the difference in partial pressure between air and sea water is one ppm.

Exactly speaking, the "one square centimeter" here refers only to an imaginary plane surface section of a column with a base of one square centimeter inside the vessel. Actually, the surface of the flowing water must be assumed not to be plane and its effective surface must increase to some extent as compared with the case of the stagnating water because of turbulence and other water movements caused by the flow. Therefore it is rather natural to find K varies with the change in the rate of water flow as given later.

2. Experimentals

1. Apparatus of Carbon Dioxide Exchange. Fig. 1 shows the scheme of experiment.

2. Flow Rate of the Air. Air including 362 ppm CO_2 is introduced from the air compressed bomb into a vessel V with a constant flow rate, 280 ml/min, through the whole experiments. The air pressure in the vessel V is 2–3 mmHg higher than the outside atmosphere. The velocity of the air flow is calculated as follows:

$$\text{Velocity of air flow}=\frac{\text{amount of air flow per unit time}}{\{\text{thickness of the air in the vessel } V(=h)\}\times\{\text{width of the air in the vessel } V(=10\,\text{cm})\}}\,.$$

3. Flow Rate of the Sea Water. The sea water was made to circulate by the gear pump G through W_1, V and W_2 with various

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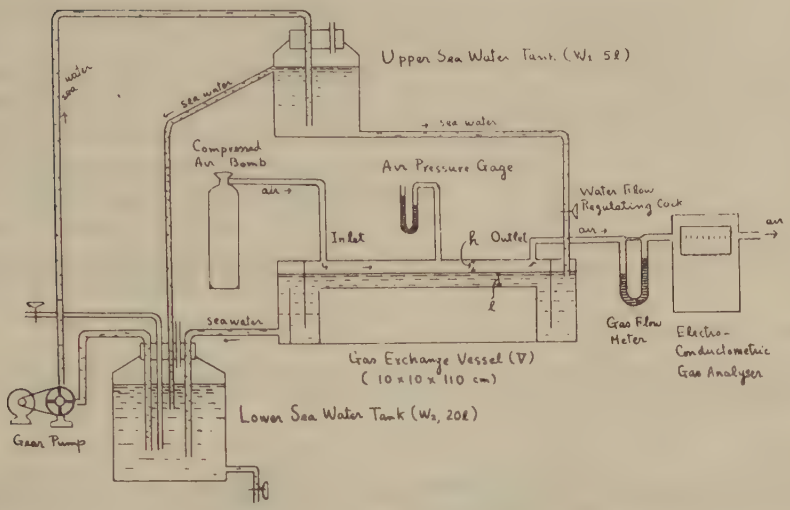

Fig. 1. Schme of Experiment.

velocities ranging 0 to 6 cm per second in the vessel V. The velocity of the flow of sea water is calculated as follows:

$$\text{Velocity of water flow} = \frac{\text{amount of water flow per unit time}}{\{\text{thickness of the sea water in the vessel } V(=l)\} \times \{\text{width of the sea water in the vessel } V(=10\,\text{cm})\}} .$$

4. Exchange time of the Air

$$\text{Exchange time of air} = \frac{\text{distance between inlet and outlet } (=d)}{\text{velocity of air flow}} .$$

5. Sea Water used. The chlorinity of the sea water used is 18.02‰ and the titration alkalinity is 226 meq/l, which is estimated by determining the total carbon dioxide in the sea water.

The partial pressure of carbon dioxide in the sea water used has previously been adjusted to various degrees. This adjustment is made by bubbling nitrogen gas or an air enriched by carbon dioxide through the sea water in the tank W_2, while the sea water is made to circulate to ensure uniformity. Another way is to add a suitable amount of 0.1 N NaOH solution to the sea water whereby the partial pressure of carbon dioxide is decreased.

6. Calculation of Partial Pressure of Carbon Dioxide in the Sea Water. The partial pressure of carbon dioxide in the sea water is calculated by using the Buch's table of chlorinity, alkalinity, temperature and pH. It is worth mentioning that there is found some discrepancy between the carbon dioxide pressure as calculated based upon the formula of Buch (1951) and the actual observed carbon dioxide pressure. This discrepancy may be caused by a possible difference between the pH standard Buch used and ours. Then the pH values observed by the present authors are provisionally subjected to correction so that the partial pressure of carbon dioxide can be calculated from these corrected pH by using the Buch's formula.

7. Determination of Partial Pressure of Carbon Dioxide in the Air. The change of partial pressure of carbon dioxide in te air in the course of the experiments is measured by using an electroconductometric gas analyser.

8. Calculation of K. K in equation (1) is calculated from the next equation (2):

$$K = \alpha \frac{2.3}{t} \log \frac{P - p_0}{P - p_t} . \qquad (2)$$

t: exchange time of air.
P: partial pressure of CO_2 in the sea water.

Table 1. Results of Experiment.

Run	Air Temp. (°C)	Thickness of the Air (h) (cm)	Velocity of Air Flow (cm/sec)	Water Temp. (°C)	Thickness of the Sea Water (l) (cm)	Velocity of Water Flow (cm/sec)	pH	P (ppm)	P_t (ppm)	Exchange time $\times 10^2$ (sec)	K 10^{-15} mole/cm² sec. ppm	Absorption (−) or Escape (+)
1	23	2	0.23	20	8	0	7.45	2102	395	4.2	3.8	+
2	23	2	0.23	20	8	0	7.45	2102	388	4.2	2.9	+
4	23	2.5	0.19	21	7.5	0	7.53	1742	405	5.2	6.3	+
9	24	2	0.23	18	8	0	7.81	837	373	4.2	4.7	+
10	24	2	0.23	19	8	0	7.84	781	373	4.2	5.3	+
11	23	2.4	0.19	18	7.6	0	7.59	1460	387	5.0	4.6	+
13	24	2.4	0.19	20	7.6	0	7.63	1351	387	5.0	5.1	+
33	23	1	0.47	19	9	0	7.43	2187	396	2.1	3.8	+
35	24	1.5	0.31	19	8.5	0	7.43	2187	402	3.1	4.5	+
37	24	2	0.23	20	8	0	7.47	2004	393	4.2	3.8	+
39	24	2.5	0.19	20	7.5	0	7.49	1908	393	5.2	4.0	+
41	24	3	0.16	21	7	0	7.52	1785	399	6.2	5.4	+
97	24	~1	0.45	22	~1	0	7.92	648	378	2.2	10	+
98	25	~1	0.45	22	~1	0	7.95	595	378	2.2	13	+
99	25	~1	0.45	22	~1	0	7.89	757	386	2.2	17	+
100	26	~1	0.45	23	~1	0	7.73	1064	396	2.2	8.9	+
14	24	~1	0.47	20	9	0	8.35	188	335	2.1	34	−
15	23	1.5	0.31	21	8.5	0	8.35	189	343	3.1	23	−
17	24	1.5	0.31	21	8.5	0	8.35	189	341	3.1	26	−
18	24	2	0.23	21	8	0	8.35	189	341	4.2	19	−
20	25	2	0.23	22	8	0	8.35	189	346	4.2	19	−
21	25	3	0.16	22	7	0	8.35	189	338	6.2	30	−
23	25	3	0.16	22	7	0	8.34	183	346	6.2	19	−
77	21	~1	0.47	21	~1	0	8.47	130	322	2.2	36	−
80	24	~1	0.47	21	~1	0	8.41	157	333	2.2	29	−
82	24	~1	0.47	21	~1	0	8.37	178	332	2.2	33	−
84	24	~1	0.47	22	~1	0	8.31	214	339	2.2	32	−
48	20	0.95	0.49	20	~1	4	7.50	1859	541	2.0	29	+
49	22	0.95	0.49	20	~1	4	7.55	1647	529	2.0	32	+
51	24	0.95	0.49	19	~1	3	7.61	1404	521	2.0	38	+
52	24	0.95	0.49	20	~1	3	7.69	1161	477	2.0	36	+
53	25	0.95	0.49	20	~1	3	7.74	1020	458	2.0	36	+
54	25	0.95	0.49	21	~1	3	7.77	926	447	2.0	37	+
55	24	0.95	0.49	22	~1	3	7.85	776	424	2.0	37	+
56	23	0.95	0.49	22	~1	3	7.95	630	413	2.0	48	+
64	23	~1	0.45	22	~1	5	8.24	264	341	2.2	46	+
70	23	~1	0.45	22	~1	6	8.05	454	331	2.2	78	+
71	22	~1	0.45	22	~1	6	7.96	580	305	2.2	58	+
72	21	~1	0.45	22	~1	6	7.88	644	281	2.2	64	+
73	21	~1	0.45	22	~1	6	7.83	733	257	2.2	63	+
57	22	~1	0.45	20	~1	2	8.36	183	336	2.2	36	−
58	23	0.95	0.49	20	~1	2	8.34	194	325	2.0	57	−
59	24	0.95	0.49	21	~1	2	8.30	220	339	2.0	40	−
76	22	~1	0.45	21	~1	6	8.47	130	301	2.2	56	−
79	21	~1	0.45	21	~1	6	8.41	157	312	2.2	52	−
81	24	~1	0.45	21	~1	6	8.37	178	313	2.2	58	−
83	24	~1	0.45	22	~1	6	8.31	214	325	2.2	56	−
85	25	~1	0.45	22	~1	6	8.25	255	342	2.2	55	−

p_0: partial pressure of CO_2 for the initial air (362 ppm).

p_t: partial pressure of CO_2 for the escaping air from the vessel V.

α: conversion factor calculating dq from dp which is the change of partial pressure atmospheric carbon dioxide in the vessel V during the time dt, $dq=\alpha dp$. In the present experiments $\alpha=h/22400\cdot(1+\theta/273)\cdot10^6$, where h is thickness of the air in the vessel V and θ is temperature of the air.

3. Result and Discussion

In Table 1 are compared the values of K at different conditions, from which the following relationships are established.

1. Relationships between K and water flow. a) When carbon dioxide escapes from the water into the air, K is found to increase linearly with increase of the rate of flow (see Fig. 2 and Table 2). b) When carbon dioxide is absorbed from the air into the water, K tends also to increase with increase in the rate of flow. However in this case the rate of increase of K with increase of the rate of flow is not so marked as in the case of escape as given in Fig. 2 and in Table 2. This appears to suggest that there is a fundamental difference between the process of absorption and the process of escape of carbon dioxide, the detail of which must be elucidated by further investigations.

Table 2. K-Value (10^{-15} mole/cm^2 sec ppm).

Velocity of sea water (cm/sec)	K (Escape)	K (Absorption
0	19—36	2.9–13
2	36—57	
3–4		29 —48
5–6	52—58	58 —78

2. Relationship between K and pressure difference of carbon dioxide between air and sea water. It is of special interest to find that at a constant flow rate of water, as shown in Fig. 3, there is a sign that K value increases when the partial pressure of carbon dioxide in the sea water approaches that of air, a fact apparently running against the authors' assumption that the carbon dioxide exchange occurs as a first order reaction. Whether this finding is correct or not, must be decided by further studies especially when the degree of the accuracy of the present determination is considered.

3. Magnitude of K value. Based on the carbon-14 content in the natural materials, Craig (1957) estimated the mean residual time of the atmospheric carbon dioxide as 7 years. If it is assumed that carbon dioxide exchange occurs as a first order reaction in nature as the authors established in their laboratory experiments, and when the corresponding K

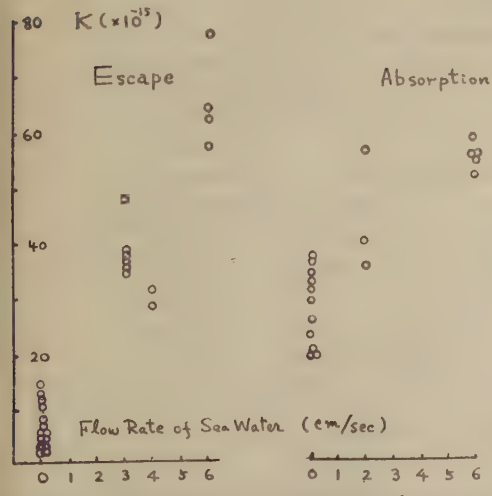

Fig. 2. Relationships between K and water flow.

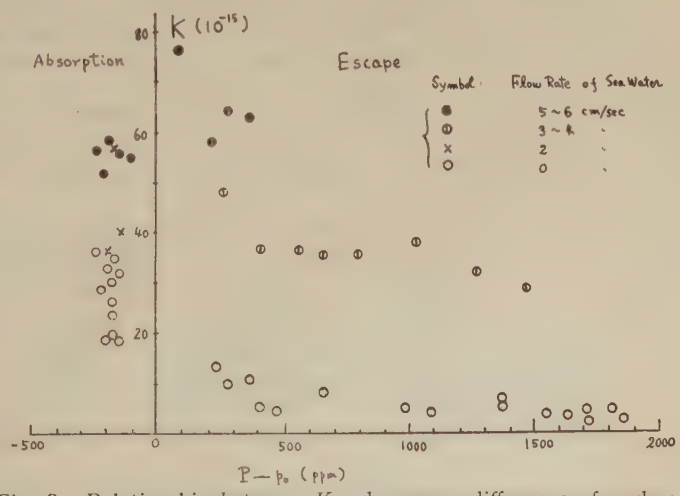

Fig. 3. Relationship between K and pressure difference of carbon dioxide between the air and sea water.

value is calculated by using CRAIG's estimation above, 2.2×10^{-13} mole/cm^2 sec ppm is obtained, a value several times the authors' K value for a rate of flow of water 3–6 cm/sec. When it is considered that in the ocean the effective surface is increased by wind and waves, it is rather natural to find greater K as calculated from CRAIG's estimation than the authors' K as determined in the laboratory.

4. Summary

In the present paper are given some preliminary results of a series of expriments regarding the carbon dioxide exchange between air and sea water flowing at various speeds. In the future the authors intend to further information concerning the carbon dioxide exchange on the conditions more closely simulating the natural circustances and to treat the results more theoretically.

Acknowledgement

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海洋魚における無機化学成分の研究—IX

海洋魚におけるアルカリ金属元素とアルカリ土類金属元素の相対量の表わし方について*

今　西　　襄**

Studies on the Inorganic Chemical Constituents of Marine Fishes–IX

On the Methods to Indicate the Relative Quantities of Alkaline Elements and Alkaline-Earth Elements in Marine Fishes.

Noboru IMANISHI

Abstract: Ca, Mg, Na and K are the main inorganic chemical constituents of marine fishes. If there is found a method by which the relative quantities of these elements are simply indicated, it will be useful to discriminate parts of fishes' bodies. The author investigated several methods and found the better one. The results are shown as follows:

1. Ca+Mg/Na+K

This ratio was calculated using four units; i.e. gram of oxide, gram of atom, gram atom and gram equivalent of these elements.

These ratios of most parts of fishes' bodies close together and accordingly these are useless to discriminate each part of fishes (see Table 1.).

2. A. $\dfrac{\text{total weight of four elements in grame quivalent } (Ca+Mg+Na+K)}{\text{ashes in gram}}$

B. $\dfrac{\text{total weight of four elements in gram equivalent } (Ca+Mg+Na+K)}{\text{total oxide in gram } (CaO+MgO+Na_2O+K_2O)}$

The method A uses the total quantity of these elements in gram equivalent per 1 g of ashes, and called specific gram equivalent of ash by the author. The method B uses the total quantity of these elements in gram equivalent per 1 g of oxide of these elements.

The values of ratios by the methods A and B distinguish part from part of fishes and these ratios are usefull to make discrimination between part and part, but the methed B is more exact than A because the total gram of oxide in 1 g of ash is differrent in each part of fishes. (see Table 2.).

The results obtained by applying the method B to parts of several marine fishes are shown in Table 4.

According to the values of ratios by the method B, parts of marine fishes are grouped to three regions as follows:

Region	Specific gram equivalent by the method B	Parts of fishes
Bone and head	36—34	bone, gills, scale, fin, head
Pyloric coeca and stomach	33—30	pyloric coeca, stomach
Liver and flesh	29—25	liver, flesh, heart, ovary, spleen, etc.

In most cases the following seems to be true. If the ratios of any two parts of a fish P

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and Q by the method B are the same, these two parts have similar constitutions of these four elements; Ca, Ma, Na and K.

If the ratio of P is larger than that of Q, the quatities of Ca and Mg in ashes of P are larger than those of Q and accorodingly the quantities of Na and K in the former become smaller than those of the latter.

アルカリ金属元素とアルカリ土類金属元素とは海洋魚における無機化学成分中，その量において首位を占める。すなわち，これら元素の酸化物としての，灰分に対する割合は最高約 60% に達する。

Ca が骨，頭等の硬質部分に多く，Mg が内臓，肉に比較的多く含まれ，アルカリ金属元素特に K が肉，内臓等に多く含まれることは概して共通的な事柄である（既報参照）[1)2)]。

しかし魚体各部分について詳細にこれら元素の量を検討すると，それぞれ異なつておる。従つて，これら元素の相対量を何等かの方法によつて表現し，これらの部分を区別することは有意義なことと思われる。

著者はこれについて種々検討した結果，比較的無難な方法を見出したのでここに報告する。

1. アルカリ金属元素とアルカリ土類金属元素の量比をもつて表わす方法

この比の値を求めることは Bishop, D. W. 等の著書[3)] に見られるがもちろん著者の目的とは異なる。

Ca+Mg/Na+K の比の値を種々の単位を用いて表わし，「かつお」の各部分について検討した。

すなわち灰分の一定量中に含まれるこれら元素の量を，それぞれの元素の酸化物としてのグラム数，または単に元素（単体）としてのグラム数，グラム原子数およびグラム当量数の4種の単位を用いて表わし，それぞれの部分について比の価を計算した。その結果を Table 1 に示す。縦軸に比の値を目盛り，魚体各部の名称をその該当する場所に記した。この表より明らかであるように，これらの表現方式によつて得られる共通な結果は，比の値が骨類部分においては大で，しかも大きい間隔をもつて分布しこれら部分の区別には好都合であるが，一方大部分を占める内臓および肉等の部分においては，この比の値が1以下に集中してその差は僅少となり，分別に困難を生ずることである。従つて好ましい表現方法とは云えない。

2. 灰分比当量方式

A 方式

$$\frac{(Ca+Mg+Na+K+)\ \text{グラム当量数}}{(\text{灰分})\ \text{グラム数}}$$

B 方式

$$\frac{(Ca+Mg+Na+K)\ \text{グラム当量数}}{(CaO+MgO+Na_2O+K_2O)\ \text{グラム数}}$$

A の方式は4元素のグラム当量数の合計を，これらを含む灰分のグラム数で除した値を求める方式である。すなわち，比の値は灰分1グラム当りの当量数に相当するので，著者は灰分比当量と名付けた。この値はまた灰分の占める金属部分の割合を示すものと考えてもほとんど差しつかえがない。何んとなれば他の金属は微量であるから。従つて，非金属部分の当量類と対比することにより，その灰の酸性度あるひは塩基性度を判断する資料ともなる。

B 方式　この方式の A 式と異なる点は分母となる灰分全量の代りに，これら元素が酸化物として存在するとした時のグラム数の合計をもつてしたもので，この場合は灰分1グラム当りの当量数とは異なるので厳密な意味での灰分比当量と云うことはできない。しかし，灰分1グラム中におけるこれら4元素の酸化物としての合量は，魚種，魚体の部分によつて異なるゆえに，灰分全量に対する割合を求めるより，これら元素の酸化物に対する割合を求めるこの方法が，より合理的である。これらの方式による結果を Table 2 に示す。

A，B 両方式とも魚体の各部分の比の値は表中適当に分散して相互を区別するのに役立つ。しかし A 方式によるよりも B 方式による方がより正しいことは上述の通りである。

Table 1. The ratios of Ca+Ng/Na+K in the ashes of *Katsuwonus pelamis*.

ratio of oxide (g)	ratio of element (g)	ratio of g. atom	ratio of g. equivalent
			24 bone (24.2)
20	20	12 bone (12.1)	22
bone (18.8)			
18	18	11	20
	bone (17.3)		
16	16	10	18
14	14	9	16
12	12	8	14
			gills (12.84)
10	10	7	12
	gills (9.16)	gills (6.42)	
8 gills (8.00)	8	6	10
6	6	5	8
head (4.95)	head (4.48)		head (6.92)
4	4	4	6
		head (3.46)	
3	3	3	4
2	2	2	2
1	1	1	1 stomach (0.92)
stomach (0.51)	stomach (0.42)	stomach (0.46)	pylo. coeca (0.60)
pylo. coeca (0.33)			
flesh (r) (0.26)	pylo. coeca (0.27)	pylo. coeca (0.3)	flesh (r) (0.46)
flesh (w) (0.16)	flesh (r) (0.21)	flesh (r) (0.23)	flesh (w) (0.34)
liver (0.14)	flesh (w) (0.16)	flesh (w) (0.17)	liver (0.26)
0 hert (0.13)	0 heart, liver (0.13)	0 heart, liver (0.12)	0 heart (0.22)

flesh (r): red flesh, flesh (w): white flesh.

Table 2. The specific gram equivalent of *Katsuwonus pelamis*.

g. eq. (Ca+Mg+Na+K) / ash (g) (method A)		g. eq. (Ca+Mg+Na+K) / oxide (g) ($CaO+MgO+Na_2O+K_2O$) (method B)	
	Scale (2.28)	36	
			gills (35.8),
20	bone (20.2)		bone (35.7)
	head (19.8)		
		35	
19			
	gills (18.8)		
			head (34.2)
		34	
18			
		33	
17			
		32	
16			
			stomach (31.7)
		31	
15			
			scale (30.8)
	stomach (14·4)		pyloric coeca (29.8)
		30	
14			
	blood (13.7)	29	
13			
			heart (28.6)
	pyloric coeca (12.5)	28	
			spleen (27.8)
12	flesh (w) (11.9)		liver (27.4)
	heart (11.7)		
	spleen (11.6)	27	
11			
	flesh (r) (10.7)		flesh (r) (26.6)
		26	flesh (w) (25.9)
10			
		25	
9	liver (9.3)		blood (24.2)
		24	

flesh (r): red flesh, flesh (w): white flesh

この方式に当量数を用いる理由は，アルカリ土類金属元素とアルカリ金属元素の量差を著しくするためである。すなわち当量数を用いるときは，アルカリ土類金属元素の量の変化はアルカリ金属元素の変化の2倍となる。

一般に海洋魚体部分においては，アルカリ土類金属元素特に Ca に富む部分は，アルカリ金属元素に乏しい傾向を有する。ゆえに当量数の間隔は著しくなり表上における分散度を良好にするわけである。

例えば「かつお」における頭と「えら」の場合について，頭に比して「えら」には酸化物1グラム当り Ca が 0.7 ミリグラム原子 (0.70×10^{-3} g·atom/1 g·Oxide)，Mg が 1.03 ミリグラム原子多く，Na は 0.30 ミリグラム原子，K は 1.40 ミリグラム原子少なく含まれる。その差は僅かに 0.03 ミリグラム原子となるが，これを当量数で計算すると，

$$(0.70+1.03)\times2-(0.30+1.40)=1.76$$

となり比当量の数値に大きい差を生じ，表上の位置が引き離され相互区分を容易にする。

3. 灰分比当量 B 方式による分布領域

深海魚の数種「かつお」，「さば」，「ぶり」，「まあじ」その他数種の海洋魚類について灰分比当量 B 方式によつて求めた結果を Table 4 に示す。

これによると骨，頭，「ひれ」，「えら」，「うろこ」等いわゆる硬質部分は，灰分比当量数の 34～36 の間にほとんど位置する。次に幽門垂，胃の部分が 30～33 の領域に，肝臓その他残りの内臓諸器官および肉が 25～29 の間に存在する。すなわち次の3領域に区分せられる。

	灰分比当量 (B)
頭および骨類領域	36～34
胃および幽門垂領域	33～30
肉および肝臓領域	29～25

Table 3. The constitution of head and gills of *Katsuwonus pelamis*.

Name of part	Ca	Mg	Na	K	Sp. g. eq.		Oxide (g) per 1 g ash
	g. atom×10^8 per 1 g of oxide				A	B	
Head	14.86	0.07	2.20	2.07	19.8	34.1	0.5803
Gills	15.50 (+0.70)	1.10 (+1.03)	1.90 (−0.30)	0.67 (−1.40)	18.8	35.8	0.5272

Table 4. Specific gram equivalents for oxides of

T.G. Eq. $\times 10^3$ per 1 g Oxide	*Katsuwonus pelamis* [Katsuo]	*Pneamatophorus tapeinacephalus* (Spring fish) [Gomasaba]	*Pneumatophorus tapeinocephalus* (Autumn fish) [Gomasaba]	*Pneumatophorus japonica* [Honsaba]	*Seriola quinqueradiata* [Buri]	*Tra tra* (larg
— 36	Gills (35.8) **Bone** (35.7)	Tail (35.7) **Bone** (35.5)			Bone and Head region	
			Bone (35.2)		**Bone** (35.5) Tail (35.4) **Head** (35.1)	Tail (35.2)
— 35		**Head** (34.9) Gills (34.8)	Gills (34.7) **Head** (34.5)	**Head** (34.5) **Bone** (34.3)	Gills, Cuticle (34.9)	**Bone** (3
	Head (34.2)				Eyes (34.4)	**Head** (3
— 34						Scale (3
				Stomach (33.7) Gills (33.5)		
— 33			**Pyloric coeca** (33.1)			
		Eyes (32.6) **Pylo. coeca** ♂ (32.5)				Pyloric coeca a
— 32						
	Stomach (31.7)		**Stomach** (31.6)			
— 31		**Pylo. coeca** ♀ (31.1)				
	Scale (30.8)	**Stomach** (30.8)				
				Pylo. coeca (30.3)		**Pylo. c**
— 30		Testes (30.0)	Blood (30.1)			
	Pyloric coeca (29.8)	Heart (29.6)				
		Spleen (29.2)				
— 29						**Flesh** (2
	Heart (28.6)	Ovary (28.7)	**Liver** (28.7)		Spleen (28.6)	
— 28			Heart (28.1)			**Liver** (2
	Spleen (27.8)			**Flesh** (27.5)	**Pylo. coeca stomach** (27.2) Pancrease (27.1)	
	Liver (27.2)	**Liver** (27.3)				
— 27			Testes (26.9)			Heart (
	Flesh (red) (26.6)	**Flesh** ♀ (26.7)	**Flesh** (26.5)			
		Flesh ♂ (26.2)			**Liver** (26.1)	
— 26	**Flesh (white)** (25.9)			(belly, back)	**Flesh** (25.9) Ovary (25.8) Gall-bladder (25.4)	
— 25						
					Testes (24.4)	**Stomac**
	Blood (24.2)					
— 24						
— 23						

$$\text{T.G.Eq. } \times 10^3/\text{Oxide (g)} = \frac{\text{total g. eq. (Ca+Mg+Na+K)}}{\text{Oxide (g) (CaO+MgO+Na}_2\text{O+K}_2\text{O)}}$$

lkaline and alkaline-earth elements in marine fishes.

urus *urus* fish)	*Trachurus trachurus* (Small fish)	*Chrysophrys major*	Deey.sea fishes	*Monocentris japonica*	*Neothunnus albacora*	T.G. Eq. $\times 10^3$ per 1 g Oxide
[Ma-aji]		[Madai]	[Ankô]	[Matsukasauo]	[Kiwada Maguro]	
						36
Gills (35.1)		Scale, Fin (35.4)	**Head** (35.7) **Bone** (35.5) Tail (35.4)	**Head** (35.8) **Bone** (35.6) (35.5) Scale		35
9) 6)		**Head** (34.8)	Fin (34.7) Gills (34.4)			
1)	**Head** (34.0) **Bone** (33.7)	**Bone** (34.0) Eyes (33.7)	[Aome-eso (34.0)] [Sokomatodai (33.9)] [Hashikinme (33.3)]			34
			[Sumikuiuo (33.0)]			33
Stomach region			[Kagokamasu (32.8)] Scale (32.6) [Fujikujira (32.4)]	**Flesh** (Cont. Bone) (32.5)		
			Gencho (31.9)			32
						31
a (30.3)			**Pylo. coeca** (30.5)			30
			Stomach (29.4) Ovary (29.3)			
9)	**Flesh** (29.0) Inner organs (28.5)				*Liver (29.1)	29
1)						28
	Liver and Flesh region					
9)		**Flesh** (26.8)		**Flesh** (27.0)	**Liver** ♂ (26.7)	27
			Flesh (26.3)			
			Liver (25.8)		**Liver** ♀ (25.9)	26
					*Liver ♂ (25.4) Ovary (t69) (25.4)	
						25
(24.4)					Ovary (t67) (24.4)	
						24
						23

* Mebachi Maguro

魚体の同種の部分でその一般の属する領域を逸脱する場合，すなわち灰分比当量数を異にする場合はその成分に異常な量的相互変化をもつておることを示すものである。

またこの値の一致するもの，近似するものはその成分の間に類似性のあることは当然であるが，しかし類値の近似が必ずしも成分の類似性を示さない場合もある。例えば一方にカルシウム分が豊富で，他方にこれが少なく，かつアルカリ金属が著しく多い場合には比当量数が偶然にもよく一致することがある。

一般にこの比当量数が上位にあることは，アルカリ土類金属元素の増加，従つてアルカリ金属元素の減少を意味する（一般通則）。

比当量数の近似が，成分4元素の相対量の近似性を示す実例を各領域について示す。

骨類領域における灰分比当量 35.5 を示す3魚種の骨および「うろこ」の成分を比較すると Table 5 のごとくなる。

次に幽門垂領域における比当量数 30.3 を示す「まあじ」(大) および「ほんさば」の幽門垂の成分を比較すると Table 6 のようになる。

次に肉領域について当量数 26.5～26.6 をもつ「かつお」および「さば」の場合を比較するとのようになる。

以上 Table 5 および Table 6 における各部分の酸化物のグラム数は，それぞれの場合ほとんど等しいのでここにあげた数値をこのまま比較し

Table 5. The constitution of bone and scale.

Name of fish and part		Ca	Mg	Na	K	Oxide (g) per 1 g ash	Sp. g. eq.
		g. atom×10³ per 1g of ash					
Bone	Buri	9.18	0.22	0.64	0.23	0.5539	35.5
	Gomasaba (spring)	8.78	0.35	0.52	0.42	0.5531	
Scale	Matsukasauo	9.18	0.24	0.80	0.26	0.5624	

Buri: *Seriola quinqueradiata*
Gomasaba: *Pneumatophorus tapeinocephalus*
Matsukasauo: *Monocentris japonica*

Table 6. The constitution of Pyloric coeca.

Name of fish	Ca	Mg	Na	K	Oxide (g) per 1 g ash	Sp. g. eq.
	g. atom×10³ per 1 g of ash					
Ma-aji (large)	0.78	1.24	4.05	3.38	0.3787	30.3
Honsaba	0.88	1.24	3.60	3.38	0.3700	

Ma-aji: *Trachurus trachurus*
Honsaba: *Pneumatophorus japonica*

Teble 7. The costitution of flesh.

Name of flesh	Ca	Ma	Na	K	Oxide (g) per 1 g ash	Sp. g. eq.
	g. atom×10³ per 1 g ash					
Katsuo (red flesh)	0.90 (1.26)	0.78 (1.10)	1.62 (2.28)	5.75 (8.07)	0.4032 (0.5685)	26.6
Gomasaba (autumn)	0.94	1.14	2.55	8.33	0.5685	26.5

Katsuo: *Katsuwonus pelamis*
Gomasaba: *Pneumatophorus tapeinocephalus*

Table 8. The constitutson of flesh.

Name of fish	Ca	Mg	Na	K	Oxide (g) per 1 g ash	Sp. g. eq.
	g. atom×10^3 per 1 g of Oxide					
Ma-aji (large)	5.62	1.45	4.00	10.65	0.5089	28.9
Ma-aji (small)	7.05	1.35	1.87	10.36	0.5418	29.0
Gomasaba (spring)	0.38	2.29	4.77	16.15	0.4534	26.2

Ma-aji: *Trachurus trachurus*
Gomasaba: *Poneumatophorus tapeinocephalus*

Table 9. The constitution of stomach.

Name of fish	Ca	Mg	Na	K	Oxide (g) per 1 g ash	Sp. g. eq.
	g. atom×10^3 per 1 g of Oxide					
Buri	0.67	1.77	9.55	12.6	0.4635	27.2
Katsuo	2.14	5.50	7.08	9.40	0.4550	31.7
Ma-aji (large)	0.39	0.30	8.77	14.40	0.4369	24.4

Buri: *Seriola quinqueradiata*
Katsuo: *Katsuwonus pelamis*
Ma-aji: *Trachurus trachurus*

ても大差はないが，Talbe 7 の場合は酸化物の量を著しく異にするので，換算値を（ ）内に示した。これらの結果をみると，4元素の相互の割合はそれぞれの場合非常によく近似する。

次に「まあじ」と「ごまさば」の肉の組成を比較すると，Table 8 のようになる。「まあじ」の大魚，小魚の肉は比当量数においてほとんど一致するが，その内容を比較すると，小魚は Ca に富み，Na に乏しい。これは一般通則よりすれば，比当量数が大魚より上位でなければならないが事実はそれほどでない。このことは Na の減少が著しいため，Ca の増加が比当量数に増加となつて現われなかつたわけである。

これは「小あじ」の肉においては Na の代りに Ca が著しく増大しておると云う異常性を示すものである。「小あじ」は成長途上の幼魚と考えられるので，あるいは成長と関係があるかも知れない。

「まあじ」の肉は，大魚，小魚とも比当量表における肉領域の上限に位置する（Table 4 参照）。このことは比当量の通則よりすると，アルカリ土類金属元素に富みアルカリ金属元素により乏しい事を意味する。肉領域に存在する代表的な「ごまさば」（春魚）の肉と比較すると，予想通り Ca に著しく富んでおりその他の元素においてはいずれも少ない（Table 8 参照）。

次に魚体の同種の部分で，その一般の属する比当量領域より著しく逸脱する場合について実例を求めると次のような場合がある。例えば「ぶり」の胃，幽門垂，また「大あじ」の胃が本来の領域を離れて肉領域に下つておることなどである（Table 4 参照）。

Table 9, Table 10 に見られるように「ぶり」の胃，幽門垂および「大あじ」の胃においては，「かつお」のそれぞれの部分に比してアルカリ土類金属元素が減少し，アルカリ金属特に K が増加して肉的性格を帯びたことを示す。すなわち灰分比当量の数値の示すところと一致する。

次に「かつお」と「ごまさば」（秋魚）の幽門垂における成分を比較すると，非常に大略的には類似するが詳細に各元素の量を検討すると「ごまさば」においては Mg が著しく増加しておる。このことが一般の幽門垂と異なる点で，比当量数の増加の原因となりこの領域の上限に位置するわけ

Table 10. The constitution of pyloric coeca.

Name of fish	Ca	Ma	Na	K	Oxide (g) per 1 g ash	Sp. g. eq.
	g. atom×10³ per 1 g of Oxide					
Buri	0.70	2.58	7.20	13.50	0.4311	27.2
Katsuo	1.43	4.61	8.25	10.30	0.4200	29.8
Gomasaba (autumn)	1.38	6.07	10.95	7.20	0.4779	33.1

Buri: *Seriola quinqueradiata*
Katsuo: *Katsuwonus pelamis*
Gomasaba: *Pneumatophorus tapeinocephalus*

Table 11. The constitution of eyes.

Name of fish	Ca	Mg	Na	K	Oxide (g) por 1 g ash	Sp. g. eq.
	g. atom×10³ per 1 g of Oxide					
Buri	13.4	0.38	5.72	1.26	0.5250	34.4
Tai (Madai)	12.8	0.26	5.15	2.36	0.5717	33.7
Gomasaba (spring)	8.10	0.62	12.00	3.14	0.5486	32.6

Buri: *Seriola quinqueradiata*
Tai: *Chrysophrys major*
Gomasaba: *Pneumatophorus tapeinocephalus*

である。

「まつかさうお」の肉において，純肉と小骨を含む肉とについての灰分比当量数を比較すると，小骨を含む肉は比当量数 32.5 を示し骨類領域に近接しておるが，純肉の場合は比当量数 27 で一般の肉の領域に存在する。すなわちこの場合においても比当量数の指示するところは正しい。

深海魚においてそれぞれが，その灰分比当量表上に占める位置については理由付けられる。すなわち「げんちよ」は深海魚中では表上において最下位を占めるが，これは肉分に富んだ魚であり，「あおめえそ」，「そこまとだい」は上方に位置するが，事実これらは骨張つた魚であることはこれを裏書しておる。

眼球について，「ぶり」，「まだい」および「ごまさば」の灰分比当量数は，それぞれ 34.4, 34.0, 32.6 である。この数値よりすれば前二者は骨類領域に属し，後者は幽門垂領域に属することになるが，実際の分析結果は Table 11 に示すようによくその事実を表わしておる。

すなわちカルシウム分は「ごまさば」，「たい」，「ぶり」の順に次第に増加し，アルカリ金属はこれと反対に次第に減少しておる。すなわち「ぶり」，「たい」，「ごまさば」の順に肉的傾向をおびて来ることが見られる。

以上の諸事実より，この灰分比当量数（B 方式による）は，概して単的に成分 4 元素の相対量を表現し，魚体各部の分別に役立つものと考えられる。従つてまたこの比当量数による魚体各部の分布領域は，未知試料の推定，分析結果の正否の判定，または成分上の特異性を知る上に有用な手がかりを与えるものと信ずる。

なお，アルカリ土類金属元素としては Sr，アルカリ金属元素としては Cs 等が成分として考えられるが，これらはいずれも極微量であるのでこの領域分布を変化せしめるものでないと考えられる。

本研究にあたつて御指導を賜つた京都大学名誉教授石橋雅義博士ならびに魚類について御教示を得た本学教授蒲原稔治博士に深謝する。

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海洋魚における無機化学成分の研究—X

海洋魚における鉄およびアルミニウムの分布について*

今　西　　襄**

Studies on the Inorganic Chemical Constituents of Marine Fishes—X

On the Distribution of Iron and Aluminum

Noboru IMANISHI

Abstract: The distribution of Fe and Al in several marine fishes were investigated. The quantities of these two elements are more than those of Cu, Pb and Zn in most cases.

Fe and Al are most found in inner organs such as liver, heart and spleen, but least in stomach and pyloric coeca. These elements are also poor in hard parts such as bone, head, gills and cuticle (scale).

Flesh contains Al more than Fe in all cases, and this fact is perhaps characteristic of the flesh. (see Fig. 1.).

The difference in relative quantities of Fe and Al in flesh can be seen in such cases that one is a part and another is the other of the same fish. For example; the belly flesh of *Seriola quinqueradiata* is richer in Al than the back, although these two parts have almost the same quantity of Fe, and red flesh of *Katsuwonus pelamis* is richer in Al and Fe than white one (see Fig. 1.).

In bones and scales Al is richer than Fe, on the other hand in gills Fe is richer than Al. (see Fig. 2.).

微量無機成分である Cu, Pb および Zn については既報[1)2)]の通りであるが，本報告は Fe および Al の分布について述べる。

Fe は血液中のヘモグロビン構成要素として動物の呼吸作用に関与する重要元素であることは周知のことであるが，Al もまたある種の酸化酵素の一成分として重要な役割をしておるようである。

Fe および Al はその量においても，Cu, Pb, Zn 等の数倍ないし数十倍にも達する。

1. 試料および処理法

試料魚は「まあじ」(大魚) を除きすべて土佐湾または浦戸湾にて漁獲せられたものである。その大きさ，重さその他一般処理法については既報[2)3)4)]に譲る。

2. 分析法

灰（乾式灰）を少量の硝酸に溶かし，稀釈して pH 1.5～2.0 とし，酸型とした陽イオン交換樹脂に通じて交換吸着せしめ，アルカリ金属，アルカリ土類金属その他をそれぞれの溶離剤（既報[5)]参照）を用いて溶出し，最後に 4 N の塩酸を通ずると Sn, Al, Fe が溶離せられる。この溶液を蒸発乾固し，残分を 0.3N 塩酸にとかして錫溶液の少量を加え（試料中に Sn の多い場合は不要）硫化水素を通じて Sn を沈澱せしめる。Sn は EDTA 滴定の際に支障を生ずるので除く必要がある。次いでこの沈澱を口去し，口液に少量の硝酸を加えて蒸発乾固し，残分を水に溶かして一定体積とする。次に EDTA をもつて Fe, Al を錯滴定[6)]する。すなわちこれを 2 分し，その一方について塩酸および酢酸ナトリウムよりなる緩衝液を用いて

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pH 3～4 とし，Cu-pan[7] (α-pyridyl-β-azo-naphthol と Cu-EDTA との混合物) を指示薬とし，EDTA 0.01 M 溶液を用いて Fe と Al の合量を求める。次に他方の液について，同じ緩衝液を用いて pH 2.2～2.5 となし Variamin blue (*n*-(*p*-methoxyphenyl)-phenylene diamine) を指示薬として Fe を滴定し，前の合量との差より Al の量を求める。

3. 結果および考察

Fe および Al のこれら海洋魚 (試料の項参照) に含まれる平均量は無機微量成分中首位を占める。また最大量を比較する場合 Cu, Pb, Zn の数倍から数十倍にも達することは前述の通りである。

魚体内における分布については，概して内臓諸器官例えば肝臓，心臓，脾臓等に多く，同じく内臓器官でも，胃，幽門垂には少ない。また骨，頭，「ひれ」等いわゆる硬質部分には少ない。(Fig. 1～Fig. 3 参照)

魚種別および部分別による分析対象数 82 件について，Fe および Al の含量がともに 5×10^{-5} グラム原子以下である部分 (微量領域) は約 60 % を占め残りの 40 % は Fe, Al のいずれか一方または両方が 5×10^{-5} グラム原子以上のものである。

Fe および Al の相対量について，両元素の当量線 (Fig. 1 参照) およびその附近にあるものは全体の約 30% を占め，当量線より上位にあるものすなわちアルミニウム分より鉄分に富むものが約 30 %，下位にあるものが約 40 % を占める。この百分率よりすれば，大略的には Al に富む部分が多いことが判る。

肉の部分について，Fig. 1 より明らかであるように，すべて当量線以下の領域にあつて，しかもアルミニウム軸に沿つて分布する。すなわち鉄分は少なくアルミニウム分が魚種および部分によつて変化するといえる。この事実は肉の特徴とも考えられる。

同一魚種の肉において部分によつて Al の含量を異にする場合がある。すなわち「ぶり」の肉には Al が一般に多いが，腹肉と背肉とを比較すると腹肉に Al が多い。また「かつお」の肉においては赤身が白身より Al に富む。しかしこの場合一方において鉄分も多くなるがアルミニウム分の増加に比べると少ない。次に「ごまさば」の肉においては春秋における季節的変化が著しく見られる。すなわち春魚には秋魚に比して Fe, Al ともに多い。しかし Fe に比して Al の増加量がこの場合においても多い。

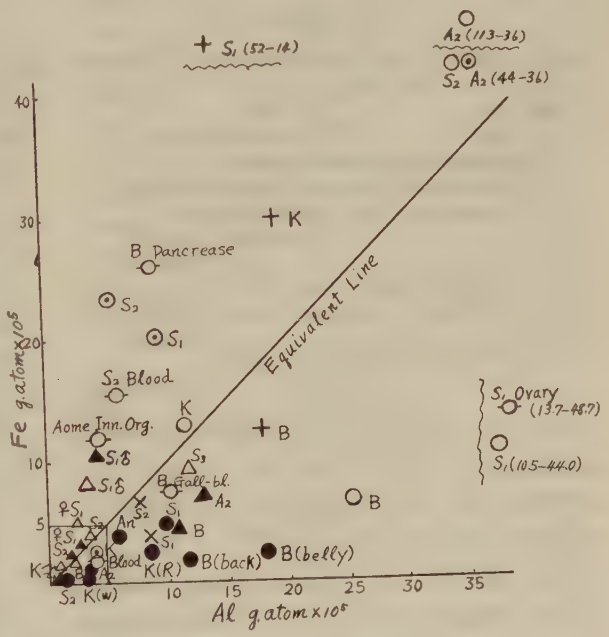

Fig. 1. Relative quantities of Fe and Al in each part of marine fishes.

●…flesh　△…stomach
▲…pyloric coeca　○…liver
(•)…heart　+…spleen
×…testes　gall-bl.…gall-bladder
K…*Katsuwonus pelamis* (katsuo)
S_1…*Pneumatophorus tapeinocephalus* (gomasaba) (spring)
S_2…　〃　(autumn)
S_3…*Pneumatophorus japonica* (honsaba)
B…*Seriola quinqueradiata* (buri)
A_1…*Trachurus trachurus* (ma-aji) (small)
A_2…　〃　(large)
An…deep-sea fish (ankô)
Aome-eso…deep-sea fish
K(R)…red flesh (katsuo)
K(w)…white flesh (〃)

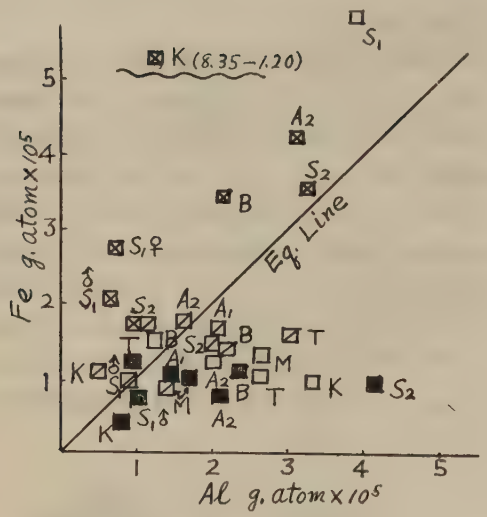

Fig. 2. Relative quantities of Fe and Al in each part of marine fishes.
■…bone ⊠…gills
⊘…head □…scale…cuticle
K…*Katsuwonus pelamis* (katsuo)
M…*Monocentris japonica* (matsukasauo)
S_1…*Pneumatophorus tapeinocephalus* (gomasaba) (spring)
S_2… 〃 (autumn)
B…*Seriola quiqueradiata* (buri)
A_1…*Trachurus trachurus* (ma-aji) (small)
A_2… 〃 (large)
T…*Chrysophrys major* (madai)

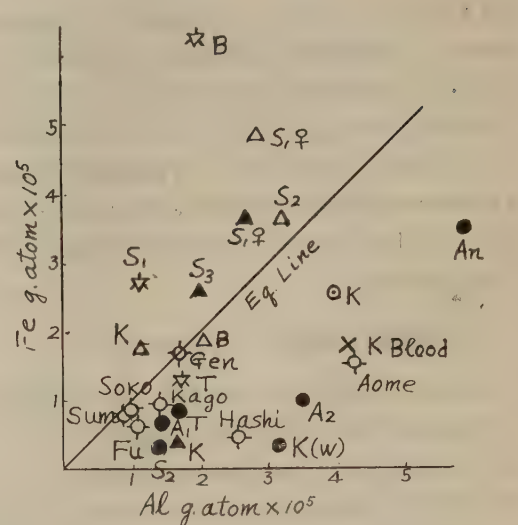

Fig. 3. Relative quantities of Fe and Al in each part of marine fishes.
●…flesh △…stomach
▲…pyloric coeca ⊙…heart
☆…eyes ⊹…deep sea fishes
K…*Katsuwonus pelamis* (katsuo)
S_1…*Pneumatophorus tapeinocephalus* (gomasaba) (spring)
S_2… 〃 (autumn)
S_3…*Pneumatophorus japonica* (honsaba)
B …*Seriola quinqueradiata* (buri)
A_1…*Trachurus trachurus* (ma-aji) (small)
A_2… 〃 (large)
T…*Chrysophrys major* (madai)
deep-sea fishes
Aome…aome-eso…*Chlorophthalmus albatrossis albatrossis*
Hashi…hashikinmedai…Gephyroberyx japonica
Gen…gencho…Areliscus joyneri
Kago…kagokamasu…Rexea prometheoides
Fu…fujikujira…Etmopterus lucifer
Soko…sokomatodai…Zenion japonicum
Sum…sumikuiuo…Synagrops japonica
An…ankô…Lophius litulon

「まあじ」,「まだい」の肉は微量領域 (5×10^{-5} g. atom 以下) に存在しておるが, 当量線より下方に位置する。すなわち鉄分よりアルミニウム分に富むことを示す。(Fig. 3 参照)

胃は「ほんさば」と「ごまさば」(春魚) の雄魚の場合 (Fig. 1) を除いてはすべて微量領域に存在する。しかも両元素はほぼ当量含まれる。「ごまさば」の春魚においてその雌雄魚は, Al の含量はほぼ同じでありながら Fe の量を異にする。すなわち雄魚の方に Fe が多い。「ほんさば」の胃において, Fe, Al ともに多いことは異例である。この胃の異常性はアルカリ金属, アルカリ土類金属の相対量においても見られる。(第9報参照[8])

幽門垂は胃と近接する器官であるが,「ごまさば」の春魚において, 雌雄魚それぞれの場合両器官の組成は大体近似する。(Fig. 1 参照)

「かつお」の場合もまた同様である。しかし一方「ぶり」においては胃は微量領域にあるが, 幽門垂は Al, Fe ともにかなり多い領域にある。すなわち近似性は見られない。

脾臓において「かつお」,「ぶり」および「ごまさば」(春魚) の場合, Al の含量はほぼ同一であるが, 鉄分に著しい差が見られる。すなわち「ぶり」,「かつお」,「ごまさば」の順に鉄分を増し「ごまさば」に至つて最も多い。

肝臓は Fe, Al ともに豊富な器官であるが, この両元素の相対量については魚種によつて全くそ

の趣きを異にする。すなわち「まあじ」の大魚においては Fe が Al に比して著しく多く，「ごまさば」の春魚，「ぶり」においてはこれと反対に Al が Fe に比して著しく多い。また「ごまさば」の春秋魚においては Al はほぼ同じでありながら，Fe の含量に著しい差を示しておるのは季節的変化によるものか否か注目せられる事柄である。

心臓においては Al に比べて Fe が多い。特に「ごまさば」において春秋魚ともに著しい。「まあじ」大魚においては鉄分は勿論であるがアルミニウム分も多い。しかし当量線より上方に位置することは，鉄分により富むことを示す。「かつお」の心臓は微量領域にあつてしかも Fe より Al に富むことは異例である。

血液について「かつお」および「ごまさば」(秋魚) の場合を比較すると，Al の量はほぼ近似しておるが鉄分において著しい差がある。すなわち「ごまさば」に Fe が多い。

Fe は血液成分の一つである故に血液中に豊富であるのは当然のように思われる。従つて心臓，「えら」等血液の集中する場所において鉄分の多いことは当然肯定せられる。(「えら」については後述する)

「かつお」の心臓における Fe, Al の量が他と趣を異にすることについては既に述べたが，これは「かつお」の血液が微量領域にあつて，しかも当量線より下方にあることに原因するものでないかと考えられる。

純粋な血液試料の採取が困難であり，且つ魚体内に内包せられる海水の混入も考えられるので，血液の組成に関する結果の正否は不明であるが，概略的相対量と考えることは差支えないと思う。当量線を離れて著しく鉄側に存在するものに「ぶり」の膵臓がある。

次に微量領域 (Fig. 2, Fig. 3 参照) に分布するものに，骨，頭，「えら」等の硬質部分があり，内臓部分としては胃がある。その他肉，幽門垂の一部がここに見られる。

骨は大体において当量線附近に分布するが，詳細に検討すると「まだい」の骨を除いて他のものはすべて線の下方に位置する。このことは Fe より Al に富むことを示すものである。

特に「ごまさば」(秋魚)，「ぶり」，「まあじ」(大魚) の骨に Al が多い。

「うろこ」においては，「ぶり」，「ごまさば」の

Table. 1. The distribution of Fe and Al in *Katsuwonus pelamis*.

Name of Part	Fe			Al		
	Order	g. atom×10⁵ per 1g ash	Fe_2O_3 (%)	Order	g. atom×10⁵ per 1g ash	Al_2O_3 (%)
Head	8	1.58	0.13	12	0.79	0.04
Gills	3	8.35	0.67	9	1.20	0.06
Bone	10	0.48	0.04	11	0.81	0.04
Scale	9	0.96	0.08	6	3.28	0.16
Stomach	7	1.76	0.14	10	1.11	0.06
Pyloric coeca	11	0.43	0.03	8	1.59	0.08
Flesh (white)	12	0.36	0.03	7	3.09	0.16
Flesh (red)	5	2.52	0.21	3	8.60	0.44
Heart	4	2.52	0.22	5	3.94	0.21
Blood	6	1.77	0.14	4	4.13	0.21
Spleen	1	29.90	2.39	1	20.25	1.04
Liver	2	112.70	1.02	2	11.50	0.59

Table 2. The distributisn of Fe and Al in *Seriola quinqueradiata*.

Name of part	Fe			Al		
	Order	g. atom×10⁵ per 1g ash	Fe_2O_3 (%)	Order	g. atom×10⁵ per 1g ash	Al_2O_3 (%)
Head	11	1.56	0.13	10	2.13	0.11
Gills	7	3.43	0.27	9	2.12	0.18
Bone	13	1.10	0.09	8	2.36	0.12
Scale	12	1.53	0.12	13	1.22	0.06
Tail	14	0.87	0.07	14	0.84	0.04
Eye	5	6.29	0.50	12	1.95	0.10
Flesh (back)	10	1.76	0.14	4	11.67	0.59
Flesh (belly)	8	2.04	0.17	3	18.24	0.91
Stomach	9	1.92	0.15	11	2.04	0.10
Pyloric coeca	6	4.44	0.36	5	10.53	0.54
Liver	4	6.45	0.52	1	25.32	1.31
Gall-bladder	3	7.31	0.58	6	10.20	0.52
Spleen	2	12.61	1.01	2	18.20	0.93
Pancrease	1	25.81	2.12	7	8.91	0.45

Table 3. The distribution of Fe and Al in *Pneumatophorus tapeinocephalus.*

Name of part	Fe			Al		
	Order	g. atom×10⁵ per lg ash	Fe_2O_3 (%)	Order	g. atom×10⁵ per lg ash	Al_2O_3 (%)
Head	7	1.75	0.14	9	1.12	0.06
Gills	6	3.54	0.28	6	3.24	0.17
Bone	8	0.94	0.08	5	4·15	0.21
Stomach	5	3.62	0.29	7	3.20	0.16
Flesh	9	0.30	0.02	8	1.38	0.07
Blood	3	15.40	1.23	3	6.05	0.31
Heart	2	23.30	1.86	4	5.50	0.30
Liver	1	41.90	3.35	1	34.40	1.75
Testes	4	6.40	0.51	2	7.95	0.41

(autumn fish)

Table 4. The distribution of Fe and Al in *Trachurus trachurus.*

Name of part	Fe			Al		
	Order	g. atom×10⁵ per lg ash	Fe_2O_3 (%)	Order	g. atam×10⁵ per lg ash	Al_2O_3 (%)
Head	5	1.79	0.14	9	1.61	0.08
Gills	4	4.22	0.34	5	3.08	0.16
Bone	8	0.81	0.07	6	2.08	0.11
Scale	6	1.26	0.10	7	1.99	0.10
Tail	9	0.75	0.06	8	1.92	0.10
Pyloric coeca	3	9.40	0.76	3	13.05	0.67
Flesh	7	0.98	0.08	4	3.46	0.17
Liver	1	113.00	9.06	1	36.20	1.84
Heart	2	44.10	3.51	2	36.00	1.83

春魚の場合を除いてはすべて当量線より下方にあつて，しかもアルミニウム軸に沿つて右方に分布する。すなわち鉄分よりアルミニウム分に富むことを示し，しかも骨より一般に Al が多いことは注目せられる事柄である。

「ごまさば」春魚の「うろこ」が当線より著しく上方に離れて存在し鉄分に富むことは一般の「うろこ」と異なる所である。

「えら」はすべて当量線より上方にあつて鉄分に富むことは一つの特徴と考えられる。特に「かつお」の「えら」において著しい。

眼球について「まだい」,「ごまさば」および「ぶり」の場合を比較すると，「まだい」においては Fe, Al がほぼ等量含まれるのに対し，「ごまさば」(春魚) 特に「ぶり」において Fe が多い。(Fig. 3 参照)

深海魚は小魚のため全体として，または内臓とこれを除く残部分とに分けて試料を作つたものであるが，その Fe, Al の相対量はいずれも微量領域にあつて，しかも当量線附近に位する。(Fig. 3 参照) しかし「はしきんめだい」および「あおみえそ」が著しく Al に富むことは例外的である。「かつお」,「ぶり」,「ごまさば」および「まあじ」における Fe および Al の分布並びに量の順位を Table 1, Table 2, Table 3 および Table 4 に示す。

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Eucampia zoodiacus EHRENBERG の分布と海況との関係*

丸茂隆三**・朝岡　治**・唐牛公平**

On the Distribution of *Eucampia zoodiacus* EHRENBERG with Reference to Hydrographic Conditions

Ryuzo MARUMO, Osamu ASAOKA and Kohei KAROJI

Abstract: The distribution of a diatom, *Eucampia zoodiacus* EHRENBERG, is closely connected with hydrographic conditions in the sea east of Japan in May 1959. This diatom is highly propagated in the coastal water characteristic of the Kuroshio warm water. It appears also far offshore in many stations of the mixing area between the Kuroshio front, in other words the Kuroshio main current, and the Oyashio front. It is not found in the oceanic water south of the Kuroshio main current, in the original Oyashio water near the land and also in two cold water masses characteristic of the Oyashio in the mixing area.

1. まえがき

Eucampia zoodiacus EHRENBERG は温帯南方性かつ沿岸性の浮遊珪藻といわれる。小久保 (1940)[1] によると，日本の内湾に広く分布し，北は北海道から南は台湾まで現われるが，量は暖海に多い。著者らの調査によると，本州東方海では主に冬から春 (3～5 月) にかけて現われ，夏から秋にはほとんど見られない。またその量は沿岸に多い。北海道から関東にいたる太平洋沿岸部のうち，黒潮の影響ある沿岸部，つまり大体金華山以南に多い。親潮接岸水が三陸沿岸に沿つて南下している場合には，普通本種はこの中には現われない。本種の分布が黒潮前線と親潮前線との間をはるか東の沖合まで続くことは珍らしくない。このように本種の分布にはつねに海況と密接な関係が見られ，まことに興味深いものがある。ここではその一例として，1959 年 5 月に採水した表面水 1/3*l* を遠心分離し，検鏡し，*Eucampia zoodiacus* の分布を求め，これと水塊および海流との関係について考察を加えた。なおこの時のプランクトン調査の概要についてはすでに報告した (気象庁海洋課，1960)[2]。

* 1960 年 11 月 18 日受理
** 気象庁海洋気象部

2. 1959 年 5 月本種の分布と海況との関係 (第 1 図)

(1) 37.3°N 以南の黒潮系沿岸水域 (35.4～37.3°N, 表面水温 16.4～19.3°C の部分，および 140°E 以西，17.2～19.6°C の部分) は本観測中最も高密で，よく本種が沿岸暖水性であることを示している。ただ房総半島に近い 3 点では全く出現せず，かつその南西の 2 点できわめて少ないのは，黒潮主流が直接ここを洗い，外洋性が強いためであろう (この 5 点は最も高温で 20.4～21.7°C)．本種は金華山沖の接岸親潮水には全く出現せず，また 37.3～40°N (6.2～13.1°C) 間の沿岸の 6 点ではきわめて少なく，この北の 3 点 (7.9～9.2°C) には全く見られない。

(2) 本種は黒潮主流以南には分布しない。主流が一つの壁となつて，本種がこれをこえて南へ運ばれるのを機械的に防いでいるためであろう。さらにこのような海況の時には，主流以南の水は外洋性が強く，ここに本種のような沿岸種が混入したとしても生存を続けるには不適でもあろう。GEK の測定結果によると (沿岸点では測定せず)，黒潮主流は 156°E 付近の沖合まで 2.5～3.0 kt の強い流速を維持している。157.5°E 付近では本種は主流より南にも分布するが，ここでは主流は

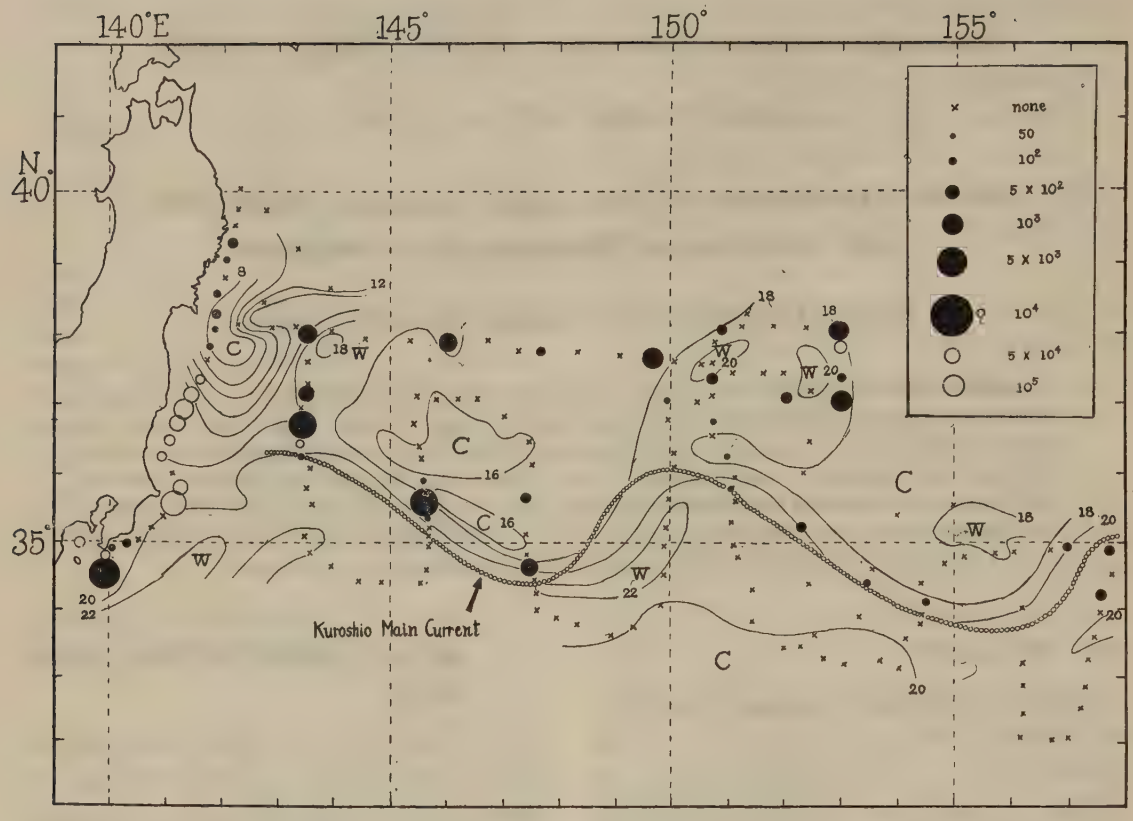

Fig. 1. Cell numbers of *Eucampia zoodiacus* in 1 *l* surface sea water and surface water temperature (°C)

1～1.5 kt と弱くなり，障壁としての作用が低下したのであろう。このように黒潮主流によつてプランクトンの分布が制約される著しい例として，小型の浮遊珪藻 *Chaetoceros radicans* SCHUTT がある (MARUMO ほか, 1960)[3]。しかし著者らは 1956 年3月 *Eucampia zoodiacus* が黒潮主流以南にかなり多量に出現している例に遭遇した（気象庁海洋気象部, 1956)[4]。この場合は主流から南にむかつて顕著な支流が分派しており，この時の分布については，海況から充分説明がついた。

（3） 本種は黒潮主流の北の海域には，観測の行われた 157.5°E までかなり普遍的に出現している。これは主として 37.5°N 以南の本州沿岸部から補給され，一部は沖合において増殖を続けたものであろう。細かく見ると，36.5°N, 146.5°E 付近（中心部 16°C 以下）および 35°N, 154°E 付近（中心部 18°C 以下）の冷水域には全く見られない。この水は親潮系であり，かつ本種が好む沿岸性をもつていず，その上ここには渦流が形成され，その中央の水は停滞していて，栄養物質の補給がなく減少し，本種の生存なり増殖なりに不適な場ができたものと思われる（これらの冷水域では，他の珪藻類も非常に少ない)。

（4） 38°N 以北（主として親潮域）については調査が行われないため，本種の分布は明らかでない。しかしこれまで行われた 1956, 1957, 1958 年の 5～6 月の調査によれば（気象庁海洋課, 1956, 1957, 1959)[5][6][7]，純粋な親潮水中にはほとんど出現せず，その分布は大体親潮以南に限られる。

3. ま と め

本州東方海の *Eucampia zoodiacus* の分布は海況とよく対応する。黒潮系沿岸水中で最も多い

が，親潮前線と黒潮前線の間の混合域にもはるか沖合まで出現する。1959年5月には本種は黒潮主流をこえて南には見られない。また純粋な親潮水中や混合域の中の親潮系冷水域にも見られない。

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元素の挙動に関する海洋化学的研究—III

内湾 おける海水中の鉄およびアルミニウムの分布
—特に潮目に関連して その 2. 須崎湾について*

今 井 嘉 彦**

Oceanographical Studies on the Behaviour of Chemical Elements—III.

Iron and Aluminium Distribution in Susaki Bay—In Connection with the Concentration of those Elements in the "Shiome" Zone.

Yoshihiko IMAI

Abstract: To make clear the distribution of iron and aluminium in Susaki Bay, southern coast in Shikoku, Japan, the author analysed them in the water samples collected from various stations and from various depths, i. e. 0,5 and 10 m. Also, the concentration of those elements in the "Shiome" zone was examined.

Results obtained are summarized as follows:

1) Iron and aluminium contents in sea water were determined, the variety in their contents among samples being recognized. That is, in iron it was from 12.8 to 226.5 γ/l. and in aluminium from 12.5 to 519.7 γ/l.

2) Iron and aluminium were more abundant in the Shiome zone than in its neighbourhood.

1. 緒 言

前報[1]に引続き，今回は須崎湾における鉄とアルミニウムの分布を明らかにした。須崎湾（水路部発行海図第 105 号参照）は野見湾を包含する湾口の比較的大きな内湾で，浦戸湾の場合とは異なり陸水による海水の汚染が比較的少なく，かつ水深が浦戸湾の場合よりも大きい（水深 8～30 m が多い）ので底土の影響を受けることが比較的少ないものと思われる。

ここでは鉄やアルミニウムを多く含む湾内固有の海水と，比較的これらの含有量が少ない外海水との混合の過程において，両元素がどのような分布上の特長を示すかを推定することが比較的に容易であると思われるので，この点をまず明らかにした。また，局部的に形成された潮目についても鉄とアルミニウムの濃縮状態を検討した。

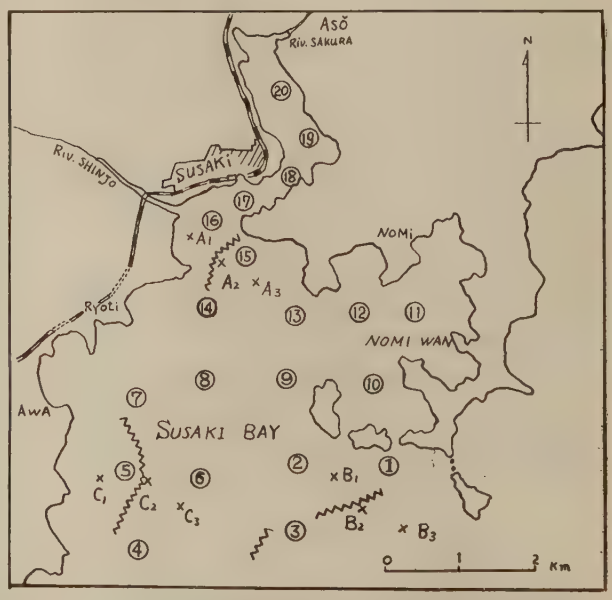

Fig. 1. Observational stations in Susaki Bay (Zigzag lines show the zone of "Shiome").

* 1960 年 9 月 28 日受理

** 高知大学教育学部化学教室 Chemistry Institute, Faculty of Education, Kochi University.

Fig. 2. Distribution of chlorinity (‰) in Susaki Bay on Dec. 6, 1958.

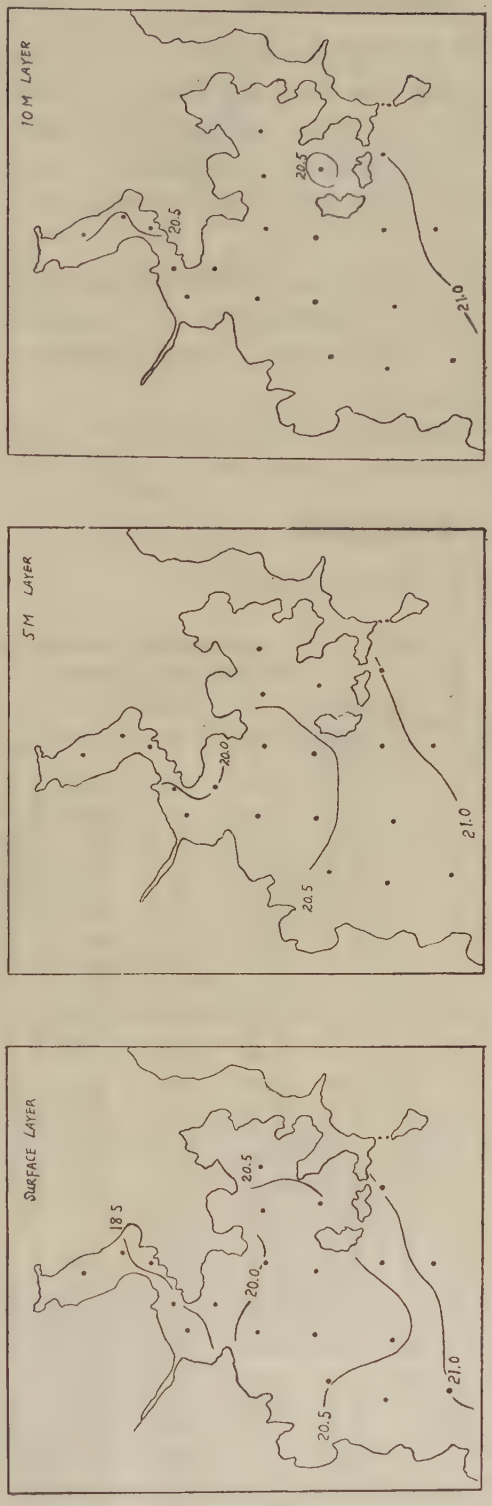

Fig. 3. Distribution of temperature (°C) in Susaki Bay on Dec. 6, 1958.

2. 試料および分析方法

1958年12月6日にFig. 1に示した地点において，表層，5m層，および10m層について採水を行つた。そのほか，表面水について目視観測により収れん線を確認し，これを追跡しつつ，潮目の海水と周辺の海水とをそれぞれ採水し分析に供した。

潮目は常に移動し，かつ収れん線の幅が相当広い場合もあつて，適確な採水を行うことが困難であつたが，多数の試料を分析したので定性的には差が論じられると思う。

試料の前処理および分析の方法は前報[1]と全く同様である。

3. 結果および考察

(1) 水温および塩素量の分布

水塊の概要を知るために，水温および塩素量の分布をFig. 2およびFig. 3に示した。各層を通じて水温は18.5～21.2°Cで，塩素量は15.43～19·30 Cl ‰であつた。

水温および塩素量の分布を鉛直的にみると，水温については21°Cを示す等温線が各層ともst. 1, 3附近にあつて，大きな移動がみられない。しかし，20.5°Cを示す等温線は深度とともに湾奥に移動し，10m層におよぶとほとんど湾全域が20.5～21°Cを占めるようになる。塩素量についても水温と同様な傾向がみられる。すなわち，高かんな外海水は水深が増すほど湾奥に向かつて移動し，湾全域を高かんな海水で占めるようになる。このことは，19.00‰の等塩素量線の移動状況から容易に知ることができる。

このように，今回観測された本湾の海水は湾奥に低温，低かんな湾内水があつて，外海水がこれ

Table 1. Iron and aluminium contents of water samples collected from several stations in Susaki Bay (Dec. 6, 1958).

Station No.	Depth (m)	Water temp. (°C)	Chlorinity (Cl ‰)	Fe (γ/l)	Al (γ/l)	Fe/Al (wt.)	Station No.	Depth (m)	Water temp. (°C)	Chlorinity (Cl ‰)	Fe (γ/l)	Al (γ/l)	Fe/Al (wt.)
1	0	21.0	19.00	49.5	81.6	0.61	11	0	20.8	19.02	44.4	40.9	1.09
	5	21.0	19.08	34.1	48.4	0.70		5	20.7	19.00	83.0	90.0	0.92
	10	21.0	19.27	56.4	59.0	0.96		10	20.8	18.97	28.2	26.0	1.08
2	0	20.9	19.05	44.1	36.1	1.22	12	0	20.4	18.95	47.0	58.2	0.81
	5	20.9	19.05	14.5	17.2	0.84		5	20.6	18.74	57.2	46.9	1.22
	10	20.9	19.05	22.2	27.0	0.82		10	20.8	18.95	85.4	50.1	1.70
3	0	21.2	19.08	84.6	162.5	0.62	13	0	20.4	18.77	200.0	12.5	16.00
	5	21.0	19.05	39.0	59.5	0.66		5	20.5	18.85	158.1	64.8	2.44
	10	21.2	19.30	501.0	388.4	1.29		10	20.8	19.00	68.3	97.6	10.70
4	0	21.0	19.00	30.5	56.4	0.54	14	0	20.4	18.97	28.2	26.0	1.08
	5	20.8	19.00	17.1	38.6	0.44		5	20.5	18.98	38.0	92.9	0.40
	10	20.9	19.26	109.4	166.0	0.66		10	20.8	19.00	84.6	63.3	1.33
5	0	20.6	18.88	74.3	61.2	1.21	15	0	19.3	18.25	35.4	52.7	0.67
	5	20.7	18.98	41.0	68.3	0.58		5	20.0	18.37	25.6	34.8	0.74
	10	20.8	19.00	117.0	121.4	0.86		10	20.8	19.00	25.6	29.7	0.86
6	0	20.2	18.68	21.3	79.5	0.27	16	0	18.8	15.13	47.0	61.5	0.76
	5	20.8	19.05	53.5	30.7	1.74		5	20.8	18.98	32.8	37.3	0.88
	10	20.8	19.00	20.5	116.2	0.18		10	20.8	19.00	86.3	105.1	0.82
7	0	20.5	18.90	51.2	94.4	0.54	17	0	18.5	18.04	217.9	311.0	0.70
	5	20.8	18.90	12.8	86.5	0.15		5	29.3	18.90	29.0	37.5	0.77
	10	20.8	19.05	47.0	90.3	0.52		10	29.4	18.65	30.7	41.8	0.73
8	0	20.2	18.66	129.9	119.7	1.09	18	0	17.5	17.55	49.5	59.6	0.83
	5	20.5	19.00	20.5	18.0	1.14		5	19.7	18.80	47.0	147.5	0.32
	10	20.9	19.00	53.8	63.4	0.85		10	19.9	18.76	26.4	33.7	0.78
9	0	18.2	19.39	32.8	36.6	0.90	19	0	18.6	18.41	195.4	241.2	0.81
	5	20.5	19.00	51.0	112.4	0.45		5	20.0	18.88	43.6	101.4	0.43
	10	20.9	19.00	94.9	63.9	1.49		10	20.2	18.90	51.2	65.0	0.79
10	0	20.2	—	64.1	66.9	0.96	20	0	18.6	18.07	105.1	115.8	0.91
	5	20.6	18.85	57.2	58.0	0.83		5	19.7	18.73	90.5	119.8	0.76
	10	20.4	18.88	54.7	87.1	0.63		10	22.0	18.41	526.5	519.7	0.01

に流入し，その流軸は時計方向に流れており，高かん域は表層からみた場合，西から東に向かつて濃度の傾斜が認められる。

湾奥の低かんな海水は，新庄川，桜川などの陸水により稀釈されたものであると考えられるが，陸水量が比較的少ない上に湾奥の水深が大きい(8～12 m)ので，この時期においては浦戸湾のように，海水塩分の著じるしい低下はなく，かつ停滞度が大きいものと思われる。

この低かんな湾内水と高かんな外海水との間には，しばしば潮目が形成される。Fig. 1 には観測された潮目の位置を示した。潮目 A は湾奥の海水と外海水との間に生じた潮目であり，潮目 B は野見湾に停滞していた低かんな海水と外海水との間の潮目で，潮目 C は沿岸水と外海水との間の潮目であると考えられ，いずれも低かんな内湾水に外海水が流入する状態の相違によつて，異なつた場所に潮目が形成される。なお，この潮目 A, B, C はそれぞれ観測した時期が異なるので相互の関係を論することはできない。

（2）　鉄とアルミニウムの分布

上述の海況下において採水した試料の分析結果は Table 1 に示した。すなわち鉄の含有量は，12.8～526.5 γ/l，アルミニウムは 12.5～519.7 γ/l であつた。この分析値にもとづいて各層における鉄の分布を Fig. 4～6 に示した。この図において水塊の移動状況に対応した鉄およびアルミニウムの分布の特長を詳細にみることは困難であるが，定性的には概略的に示した等濃度線の状態からある程度推定することができるものと思われる。

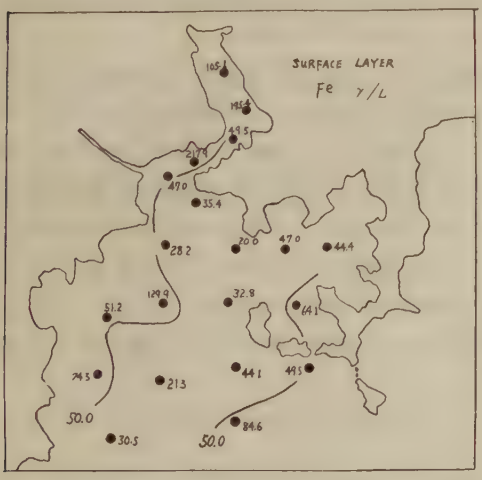

Fig. 4. Horizontal distribution of iron at the surface layer.

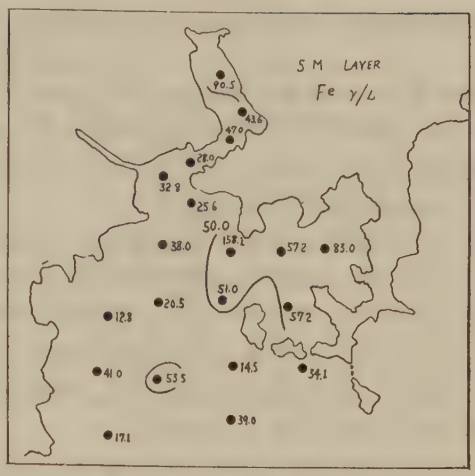

Fig. 5. Horizontal distribution of iron at the 5 m. layer.

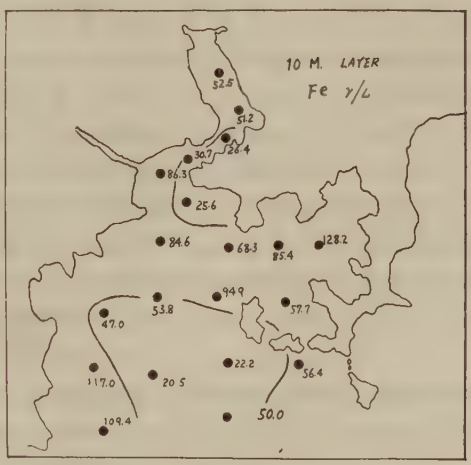

Fig. 6. Horizontal distribution of iron at the 10 m. layer.

Fig. 4 は表層における鉄の分布を示した。すなわち，湾の中央部には 20～30 γ/l の値を示す海水があり，沿岸に近いところには 50 γ/l 以上の値を示す海水がある。特に st. 17～20 の湾奥部は大きな値を示している。

Fig. 5 は 5 m 層における鉄の分布を示した。この層における鉄の分布の特長は，鉄の含有量の少ない外海水が大きく流入して湾奥に近い st. 17 附近にまで達し，そのため 50 γ/l の値を示す等

濃度線は湾奥から野見湾に至る区域に移動している。

Fig. 6 は 10 m 層における鉄の分布を示した。すなわち，50 γ/l 以下の値を示す海水は 5 m 層の場合ほど湾奥まで流入しておらず，湾の沿岸にそつて鉄の含有量が多くなつている。

以上，表層，5 m および 10 m 層を通じて考えられることは，外海水中の鉄の含有量は内湾水と比較して少なく，Fig. 2 に示した塩素量の分布から知られるように外海水が時計方向に流入すると，これに伴なつて鉄の含有量の少ない区域も次第に湾奥におよぶようになる。

また鉛直的にみると表層と 5 m 層とがこの傾向をあきらかにあらわしている。10 m 層の分布においては 50 γ/l の等濃度線が湾口に向かつて移動しているようにみえる。これは塩素量についての 19.00 ‰ の等塩素量線が湾奥にまで達し，湾全域が外海水で占められていることと考え合わせて矛盾するように見えるが，沿岸に近く，しかも浅いところの海水が鉄の大きな値を示しているので，恐らく 10 m 層においては底土の影響があらわれはじめたことを示すものではないかと考えられる。湾奥の st. 17～20 の海水は停滞し鉄が濃縮される傾向を示している。

アルミニウムの分布についても st. 17～20 の海水が表層，5 m および 10 m の各層を通じて相対的に高い値を示していることは鉄の場合と同様

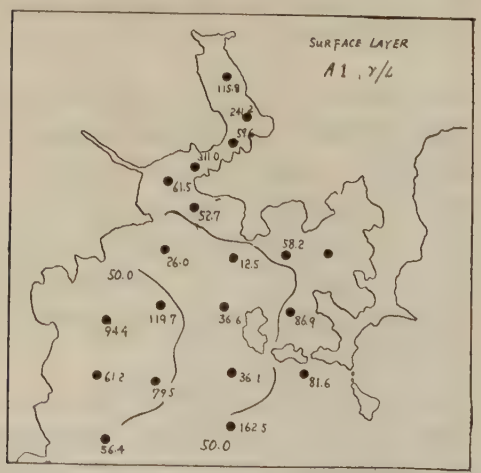

Fig. 7. Horizontal distribution of aluminium at the surface layer.

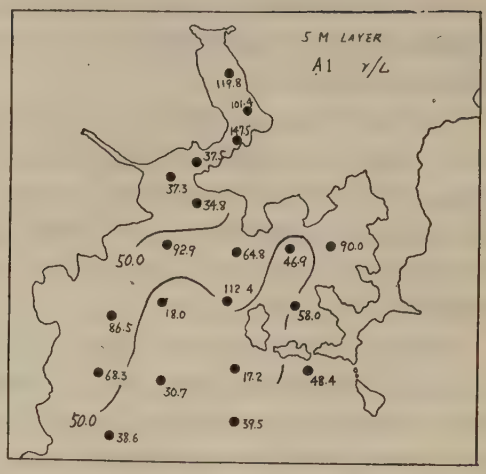

Fig. 8. Horizontal distribution of aluminium at the 5 m layer.

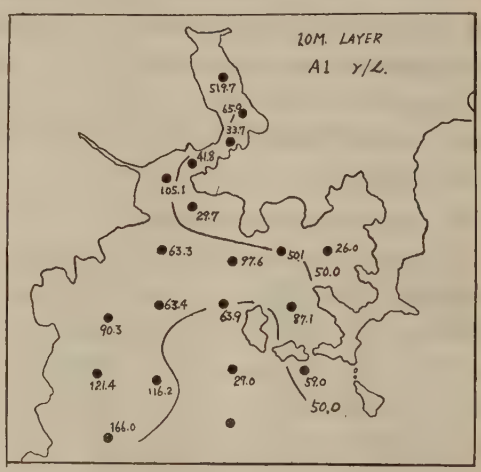

Fig. 9. Horizontal distribution of aluminium at the 10 m layer.

である。その他の傾向も概して鉄の分布に似ている。各層の分布は Fig. 7～9 に示した。アルミニウムの分布において鉄の分布と明らかに異なる傾向はみられない。ただ st. 15, 16 が 5 m 層において低い値を示していることは注目に値する。鉄の 10 m 層における分布についても st. 15, 16, 17 がわずかに小さい値を示している。これらの原因については明らかでなく，今後なお検討を要す。

（2） 潮目の海水における鉄とアルミニウムについて，

潮目において鉄とアルミニウムが濃縮される傾向を示すことは前報[1] において指摘したが，この

Table 2. Iron and aluminium contents of water samples collected from several stations at the "Shiome" and its neighbourhood in Susaki Bay (Dec. 7, 1958).

Station No.	Depth (m)	Water temp. (°C)	Chlorinity (Cl ‰)	Fe (γ/l)	Al (γ/l)	Station No.	Depth (m)	Water temp. (°C)	Chlorinity (Cl ‰)	Fe (γ/l)	Al (γ/l)
A_1	Surface	20.2	15.27	42.6	46.3	A_1	5	20.3	18.95	30.2	42.3
* A_2	〃	19.8	18.52	122.8	143.2	* A_2	〃	20.0	18.76	54.5	46.5
A_3	〃	20.5	18.93	74.4	65.7	A_3	〃	20.2	18.36	32.1	37.8
B_1	〃	20.9	19.00	30.3	27.5	B_1	〃	20.3	19.05	13.3	16.4
* B_2	〃	20.4	19.05	48.6	73.4	* B_2	〃	20.3	19.00	17.4	21.0
B_3	〃	21.4	19.13	19.3	12.4	B_3	〃	20.2	19.00	34.6	26.3
C_1	〃	20.7	18.86	101.2	65.5	C_1	〃	20.3	18.97	34.6	18.8
* C_2	〃	20.4	18.73	135.5	86.8	* C_2	〃	20.5	19.00	44.3	62.1
C_3	〃	20.7	18.88	45.8	73.4	C_3	〃	20.2	19.01	33.1	25.5

* Collected at the "Shiome".

要因については種々考えられる。すなわち，沿岸附近では下降流によつて収れん線に懸濁物や浮遊物が多く集まり，これに鉄やアルミニウムが吸着などによつて濃縮される場合である。また，底層水のうち，底土にきわめて近い海水のなかには鉄およびアルミニウムを多く含んでいるが，この底層水がいわゆる上昇流などによつて表層に運ばれる場合も考えられ，いずれも潮目における元素の濃縮に関与する要因として注目しなければならない。

したがつて本湾では底土の影響が比較的少ないものとみて，潮目における鉄とアルミニウムの濃縮状態を，潮目における海水と周辺の海水との鉄とアルミニウムの含有量を比較することによつて推定した。

分析の結果は Table 2 に示した。すなわち，表からわかるように鉄もアルミニウムも潮目においてわずかに高い値を示し，この分析法による誤差 $\pm 0.5\gamma/l$ を考慮してもなおわずかに高い。したがつて，両元素が潮目の海水に濃縮されていることをうかがうことができる。しかし，5 m 層では逆に小さな値を示す場合もあつて，この現象が主として表層水においてみられることを示しているように思われる。しかし 5 m 層における不連続面での sampling が困難であつたので，この問題はなお検討を要するが，以上の事実から，本湾の潮目における鉄とアルミニウムの含有量が多いことは，下降流の収れん線にこれらの元素が種々な浮遊物や懸濁物とともに濃縮されているものと推定される。

本研究を行なうに当り終始御指導と御鞭達を賜つた京都大学石橋雅義名誉教授および高知大学山本広志教授に深く感謝します。

文　献

1) 今井嘉彦 1960: "元素の挙動に関する海洋化学的研究II" 日本海洋学会 **16**, 167.

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Correspondence

Comments on the paper "Western Boundary Currents and Vertical Motions in the Subarctic North Pacific Ocean".*

F. C. W. Olson**

The paper on "Western boundary currents and vertical motions in the subarctic North Pacific Ocean" by Jotaro Masuzawa which appeared in the June 1960 issue of this Journal impressed me as a notable contribution to the oceanography of this important area. There are two comments I would like to make which may provide further support for the conclusions obtained by Masuzawa.

In the first place, I was struck by the fact that no mention was made of the effect of the excess of precipitation over evaporation in this area. This matter can be settled quite readily by reference to Jacobs (1951). From this we find that the area north of the 40°N parallel is 14.9×10^{16} cm^2. The mean annual excess of precipitation over evaporation is estimated from Jacobs' Figures 46 and 47 to be roughly 40 cm/year. The net southward transport across the 40'th parallel is thus somewhat less than 2×10^{11} cm^3 sec^{-1}, which is less than 1/40 of the value computed by Masuzawa and therefore of little significance in the over-all effect.

It is interesting that the qualitative study by Muromcev (1958) on the general circulation in the Pacific agrees completely with the more detailed findings of Masuzawa. Muromcev indicates not only a northward current at 2500 meters in the western part of the Pacific but also mentions ascending currents in the intermediate waters.

Finally, I must express my pleasure in the detailed calculations on vertical velocities given in this paper. Vertical velocities have been neglected too long by oceanographers. The more data we have on this subject, the sooner will we have a proper understanding of oceanographic phenomena.

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Jacobs, W. C., 1951: The energy exchange between sea and atmosphere and some of its consequences. *Bull. Scripps Inst. Ocean.*, Vol. 6, No. 2, pp 27-122.

Muromcev, A. M., 1958. Scheme of general circulation of the Pacific Ocean waters. *Izv. Akad. Nauk. SSSR. Geographic Series*, 1958, 4, pp 24-32.

* November 17, 1960.

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Masuzawa's reply

It seemed to be clear that the effects of both precipitation and evaporation are negligibly small in the water budget which is considered in my paper, comparing with the transports in the ocean. However, as Mr. Olson pointed out, I should have presented the estimation of the order roughly.

I did not know the paper of Muromcev on the general circulation in the Pacific. I would like to appreciate Mr. Olson for his friendly comments and informations.

Comment on the paper "Western Boundary Currents and Vertical Mortions in the Subarctic North Pacific Ocean", by Jotaro Matsuzawa in Journal of Oceanographical Society of Japan **16** (2).

Takashi Ichiye*

This paper deals with interesting features of vertical structure of the western boundary current near northern Japan. Masuzawa derived the total volume tronsport of the western current by use of the method developed by Stommel (1956). Similar procedure was applied by myself to determine transports in the upper and lower layer in the ocean divided by an arbitrary interface (Ichiye, 1960a). In the North Pacific this procedure works well in obtaining water balance in a region surrounded by coasts and latitude circle, because there is almost no transport through Bering Strait.

Although the procedure can be successfully applied in determining a large scale feature of water budget in the ocean, particular care should be taken in its application in deriving detailed vertical structure of the current. The total transport across a section between two stations on a latitude circle is essentially determined by the integral of wind stress curl between the stations. The most important thing in applying the method to actual oceans is to have a good estimate of mean values of the wind stresses over the ocean, to which the results, particularly structures of vertical currents are quite sensitive, as pointed out later by Stommel and Arons 1960). The particular latitude, 40°N chosen by Masuzawa,

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unfortunately, happens to be most vulnerable to two kinds of sources of errors in estimating wind stress curl.

The integral of wind stress curl along a latitude circle is divided into two parts like

$$\int_a^b \mathrm{curl}\,\tau dx = \int_a^b \frac{\partial \tau_y}{\partial x} dx - \int_a^b \frac{\partial \tau_x}{\partial y} dx$$

$$= \tau_y(b) - \tau_y(a) - \int_a^b \frac{\partial \tau_x}{\partial y} dx \qquad (1)$$

in which x and y are coordinates directed to the east and the north, respectively, and a and b are x-coordinates of two stations. Generally the part of the integral including $\partial\tau_x/\partial y$ is more important than the part due to τ_y. The values of $\partial\tau_x/\partial y$ might be fairly accurately determined from the tabulated data of wind stresses for 5 degree squares (for example; HIDAKA, 1958) along the latitudes where τ_x is almost a linear function of y. (The latitudes between 20°N to 35°N where subtropical easterly winds change to westerlies satisfy this condition). According to HIDAKA's table, maximum values of τ_x are found at 37.5°N in winter, 42.5°N in spring and 47.5°N in autumn (there is no definite maximum in summer, owing to weak westerlies). In the annual mean, two maxima of τ_x in the westerly are seen at 47.5°N and 42.5°N. This implies that τ_x is not a linear function of y near the latitude of 40°N and thus the gradient $\partial\tau_x/\partial y$ determined from values of τ_x tabulated at 5 degree intervals is not accurate.

Another source of errors in MASUZAWA's calculation of wind stress curl is that the integral (1) along 40°N shows a large amplitude of annual variations. The results of calculation based on Hidaka's table are tabulated in Table 1, in which the integral of (1) is shown for different seasons, in western (150°E to 175°W) and eastern (175°W to 130°W) section and for two parts due to $\partial\tau_y/\partial x$ and $\partial\tau_x/\partial y$. This table indicates that the total transport across 40°N is directed to the north in winter, owing to the strong shear of the westerlies in the western section, quite contrary to MASUZAWA's result which is obtained from the annual mean wind stresses. (The individual values of the integral $\int(\partial\tau_x/\partial y)dx$ in the table may be not accurate as discussed above, but we are concerned with their seasonal change). His data of hydrographic stations were obtained in summer and early autumn. Although the summer value of the integral (1) is close to the annual mean value adopted by him, there is a possibility that the transport may be about twice his value for the western boundary section which was occupied in September. Under such circumstances, his elaboration in calculating vertical currents at each level for west and east sections is hardly justified, since he combined several sources of data obtained at different periods of time.

Incidentally, two problems may be imposed on

Table 1. Integral of wind stress curl 40°N. $(\rho\beta)^{-1}\int \mathrm{curl}\,\tau dx (10^6\ \mathrm{m^3/sec})$

	Western Section			Eastern Section			Total Section
	A	B	A+B	A	B	A+B	
I	8.3	10.7	19.0	−0.9	−2.1	− 3.0	16.0
II	1.6	−4.5	−2.9	−2.3	16.5	−18.8	−21.7
III	0.7	−1.1	−0.4	−5.4	−3.9	− 9.4	− 9.8
IV	0.0	−5.3	−5.3	−0.2	−8.8	− 9.0	−14.3
V	1.5	0.8	2.3	−2.2	−8.0	−10.2	− 7.9

I, Dec. Jan. Feb.; II, Mar. Apr. May; III, June Jul. Aug.; IV, Sept. Oct. Nov.; V, Annual mean.
$A=(\rho\beta)^{-1}\int(\partial\tau_y/\partial x)dx$, $B=(\rho\beta)^{-1}\int(\partial\tau_x/\partial_y)dx$

deep water circulation in the area concerned. One problem is to determine the response of transport of the western boundary section to the seasonal change of the integral (1) along the latitude circle as shown in Table 1. Particularly it is interesting to see how the transport may change in winter. For this problem the same section must be surveyed at least each season of the year. (In such surveys, intervals of sampling layers below 2000 m should be taken at about 300 m as in many Atlantic surveys carried out by Woods Hole group, because transport below 2000 m is sensible to slight changes in density structure in dynamic calculations).

Another problem is related to the counter current under the Kuroshio flowing eastward 30°N and 40°N. Transport of the counter current which is directed to the west has almost the same amount as that of the Kuroshio above the depth of 1200 m (45×10^6 m³/sec versus 56×10^6 m³/sec; ICHIYE, 1960b). On the other hand, transports below 1200 m in the western boundary sections are all directed to the north from 15°N to 45°N (ICHIYE, 1960a). Therefore, it

is expected that the counter current approaching the coast might increase the northward transport between 30°N and 40°N. But actually the transport in the lower layer of the western sections does not show such an increase within a range of these latitudes (figure 8; ICHIYE, 1960a). This inconsistency may partly be due to the condition that my calculation of transports is based on the annual mean of wind stresses and hydrographic data distributed at random in regard to season. However, there are two mechanisms that may explain such inconsistency. One mechanism is that the excess of the water transported into the lower layer of the western boundary region by the counter current is removed upward through interface. The other mechanism is that the excess water may flow back to the south near the coast and escape the estimation of transport in the network of stations. This question might be again solved by taking a close network of deep sea stations at suitable places near Japan.

The oceanographic data in the vicinity of Japan heretofore are notoriously disorganized in spite of their abundance, because very few hydrographic cruises were operated strictly on the basis of scientific interests in the past. I hope that such situation will be improved and more reliable data will become available in this very imporatant area.

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MASUZAWA's reply

Unfortunately I had not had an opportunity to read the instructive papers, "On water budget in a two layered ocean" by ICHIYE nor "On the abyssal circulation of the world ocean I, II" by STOMMEL and ARONS before I prepared the manuscript of my paper.

I recognize that there will be a possibility of having fairly serious errors in the calculation of the wind stress curl on the 40°N latitude, because I employed only the wind stress values tabulated at five degrees intervals. And also, the transport of the western boundary zone may change considerably in response to the seasonal change of the wind stress curl, but unfortunately we have had no suitable data. Therefore, as the first step of the investigation, I took no heed of the season when the hydrographic stations were occupied and I adopted the annual mean of wind stress curl, in order to obtain roughly the average structure of deep water motion in the subarctic North Pacific. However, it might be true that this procedure will be probable to lead to a misleading idea about that. I hope that the conclusion of mine could be accepted as hypothetical one based upon the assumptions and procedures which are not satisfactory but still be valid to the first order of approximations.

Of course, I agree with ICHIYE on an opinion that our hydrographic observations in the past were not quite satisfactorily organized. During these years we have been trying to take the suitable network of deep-sea stations and to improve the selection of intervals of sampling layers in the deep water as much as possible. We regret, however, that the matters have not yet become much improved. At last, I would like to acknowledge Dr. T. ICHIYE for his frank comments and advice.

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寄　稿

昭和34年東北海区綜合海況

安　井　善　一

昭和 35 年 12 月 7・8 日函館市において開催された第 10 回東北海区海洋調査技術連絡会において，東北海区水産研究所，海上保安庁水路部，第 1，第 2 管区海上保安本部，気象庁海洋気象部，函館海洋気象台その他の関係者が昭和 34 年における東北海区の海況について，協議取りまとめた結果，次の結論を得たので御参考に供します。

昭和 34 年東北海区綜合海況（第 10 回東北海区海洋調査技術連絡会で審議とりまとめた）

月＼海域	黒潮域	混合域（黒潮前線と親潮前線の中間の海域）	親潮域	津軽暖流域
2月（1月下旬を含む）	黒潮主流の北上端は 36.5N，144E にあり，そこから 33.5N，147E 付近までは南東流し，これから反転北上し 36.5N，148E 付近から東に転向していた。 この流路は 1955 年 5 月に似ていた。	金華山南東沖合に孤立しかけた暖水塊，39.5N，144.5E 付近に小規模な孤立暖水塊，39N，148.5E 付近に大規模な暖水塊（T200：12°C）があつた。	親潮接岸分枝は38.5N，143E 付近まで南下してから東に向い，145E 付近から更に南下して黒潮北縁に流入していた。親潮沖合分枝は 42.5N，148.5E 付近から南西に延び，その一部は 145E 付近で前記の接岸分枝に合し，一部は反転して東ないし北東に流れ去つた。	津軽暖流の張り出し範囲は 143E に達していた。
3月	関東東方沖の黒潮主流は 142E 線上で 35.3N 付近にあつた。	143E 以西の混合域は 35.5N 付近から 39N 付近までの範囲を占めていた。	黒潮接岸分枝の状況は 2 月と同様であつた。	津軽暖流は三陸沿海を金華山付近まで南下していた。
5月	黒潮主流の北上端は 36.5N，144E 付近にあつた。 黒潮主流の蛇行の山は 143，151E に，谷は 148，155E にみられ，GEK による最大流速は沿岸域では 3.7kt，沖合では 3.1 kt で，157E 以東には 2 kt 以上の流速はみられなかつた。	38N，145E 付近に暖水塊（T100：16°C），36.5N，145E 付近に冷水塊（T100：6°C）があつた。 37N，152E 付近に孤立暖水塊（T100：18°C），37.5N，145.5E 付近に暖水塊（T100：16°C）があり，後者の先端は 41N，143E で T100：8°C を示していた。35N，147.5E 付近に冷水塊があつた。	親潮接岸分枝は 37N まで南下していた。 親潮接岸分枝は 40N 付近では明瞭でないが，冷水域（T100：6°C）が 39N，144E 付近から金華山沿海を経て 36.5N，142E に達していた。親潮沖合分枝は 40N，145E まで南下していた。	
6月前半	黒潮主流は 144E 付近で 36N，151E 付近で 36N を通つていた。	37N，152E 付近の暖水塊は 5 月後半と同様であつた。37.5N，144E 付近に暖水塊（T100：16°C），36N，143E 付近に小冷水塊（T100：7°C）があつた。		津軽暖流の張り出し範囲は 142E 付近までであつた。
6月後半	黒潮主流の北上端は 35.8N，143N にあつた。	38N，145E 付近に暖水塊（T100：15°C）があつた。前期の冷水塊は 36.5N，144 付近に移動し T100：10°C を示していた。		
7月前半	黒潮主流の北上端は 36N，144E にあつた。	38N，144.5E 付近に暖水塊（T100：15°C），38.5N，142.5E 付近に冷水塊（T100：6°C），また 36N，144.5E 付近に前期の小冷水塊（T100：12°C）がみられた。		

7月後半	黒潮主流の北上端は 36N，143E にあつた。	38N，145E 付近の暖水塊は北西に延びて 40N，143.5E に達していた。38N，143E 付近に冷水塊（T100:6°C）があつた。	42.5N，144E 付近に小規模な暖水塊（T100:8°C）があり，この水塊域を除く距岸 60 浬以内に親潮冷水（T100:2°C 以下）がみられた。	津軽暖流の張り出し範囲は 143E に復したが，南部へのふくらみはまだ顕著でなかつた。
8月前半	黒潮主流の蛇行の山は 36.5N，144E および 37.5N，151E にあり，谷は 34.5N，147E にあり，総じて流軸は前期よりやや北方に移動していた。	38N，145E 付近に暖水塊（T100:15°C）があり一部は北方に延び中心位置は 5 月よりやや東偏した。また 38.5N，152E 付近から西方に延びた暖水域はその先端の 39N，146E 付近から北方に延び親潮域にまで達していた。	親潮接岸分枝は 143E 線に沿つて南下していた。親潮沖合分枝は 145E に沿つて南下し，39N，146E 付近では巾が狭くなつていたが，更に南方に延び黒潮主流の北側の冷水塊に連つていた。	7月後半と同様であつた。
8月後半		暖水塊（T100:12°C 以上）が 144E 線に沿つて北上し 41N に達していた。親潮前線は 145～150E の範囲ではほぼ 40N 線上にあり，154E 付近では 42.5N 付近まで北上していた。	親潮接岸分枝は 38.5N，142.5E まで南下していた。	津軽暖流の張り出し範囲は 143E に達していた。
9月		40.5N，143.5E に暖水塊（T100:16°C）があつた。	親潮沖合分枝は 39N，144E まで南下していた。	
10月		暖水塊が 39N，144E 付近（T100:16°C）と 39.5N，142.5E（T100:17°C）にみられた。	40N，145.5E に親潮沖合分枝の先端がみられた。	
11月前半	黒潮主流の北上端は 36.7N，144E にあつた。主流の南側の 34.5N，143.5E 付近に反時計廻りの渦流がみられた。	38～39 N，143～144 E に暖水塊（T100:15°C）があつた。	親潮接岸分枝の先端は 39.5N，143E に達していた。	
11月後半（12月上旬を含む）	黒潮主流の位置は11月前半とほぼ同様であつた。	41N，144E に暖水塊の先端（T100:8°C）がみられた。	親潮接岸分枝の状況は11月前半とほぼ同様であつた。	津軽暖流の張り出し範囲は 143E を越えていた。
全年の特徴	黒潮主流は1年を通じて比較的蛇行が大きく，144E 線上でのその北上端は 36～37N の間に，また 146～148E の間でのその南下端は 33.5～34.5N の間にあり，全体の流軸は1955年以降最も南偏していた。このため34～38Nの海域の表面水温は1年を通じて平年並かやや低目の傾向を持続していた。	金華山沖合には徐々に孤立暖水塊が形成されつつあつた。	親潮冷水（T100：2°C 以下）は1年を通じて南下は弱く，その範囲は 1955 年以降最も狭かつた。親潮域の表面水温はこの1年を通じて7月を除き平年並かやや低目で，特に8月は低目であつた。	津軽暖流の張り出し範囲は2月には平年並，5月には平年よりかなり狭く，8月には広くなり，11月には平年並に復して，1年を通じて変動が大きかつた。

録　　事

1. 月例会

（1） 12月例会（12月13日，於東大）

1. 極海の深層循環とこれの関連した深層流　福岡二郎(気象研)　2. Salinity Change in Alligator Harbor and Ochlockonee Bay, Florida 市栄誉他（The Florida State University）（吉田代読）

（2） 1月例会（1月17日，於東大）

1. 大循環　高野健三(東大)　2. 赤道湧昇流の計算　日高孝次(東大)

2. 評議員会議事録

（1） 1月評議員会（12月6日，於東大）

出席者（順不同）竹内能忠，岩宮政雄，須田暁次，吉田耕造，佐々木忠義，日高孝次，平野敏行，宇野木早苗　丸茂隆三，半沢正男，宇田道隆

○決定・処理事項

（a） 日本学術会議地球物理学研究連絡委員会海洋物理学分科会委員候補者推薦の件

先に行つた会員よりの投票結果は次の通りであつた。

総投票数	132		
吉田　耕造	91	次点	
増沢譲太郎	60	宇田道隆	35
中野　猿人	57	南日俊夫	34
庄司大太郎	53		
竹内　能忠	52	以下省略	
日高　孝次	42		
佐々木忠義	39		
小野　弘平	38		
福岡　二郎	38		
半沢　正男	38		

この選挙の結果に基づいて評議員会は高点者10名を日本学術会議地球物理学研究連絡委員会海洋物理学分科会に推薦する事に決定した。

（2） 12月評議員会（12月13日，於東大）

出席者（順不同）日高孝次，宇田道隆，松江吉行，須田暁次，宇野木早苗，岩宮政雄，増沢譲太郎，吉田耕造，平野敏行，丸茂隆三，福岡二郎，南日俊夫

○決定・処理事項

（a） 春季大会の件（丸茂評議員）

○昭和36年春季大会は4月～5月とし，神戸を第一候補，東京を第二候補とする。

○講演申込み締切りは2月20日

○プログラムは今まで通り，アブストラクト付きガリ版印刷

○プログラム及び評議員投票用紙の発送は3月5日頃

○環境シンポジウムは，4月8日水産学会と共催で行い，内容については，宇田副会長，松江，平野評議員及び会合係（丸茂評議員）に委任。

○特別講演は適当なものがあれば行う。

（東京が会場の場合

i） 会場は順序からいつて東京水産大学

ii） 会場を二ケ所に分けて行い，開期は4月3，4日の2日間とする。会場の分け方については丸茂，半沢会合係が原案を作り，1月の評議員会に提出する。

iii） 評議員会は4月3日

iv） 懇親会は4月4日

○今まで春の大会は，水産学会開催期の前後につけて行つていたが，この開催の時期につき，春の大会の折，全会員にはかる。

（b） 図書交換の件（平野評議員）

ドイツの Senchenbergische Naturforschen der Gesellschaft からの Abhandlungen と会誌の交換をする事が認められた。

（c） 新入会員の件（丸茂評議員）

次の二氏の入会が認められた。

広沢徳蔵（新潟県水産試験場）

朱　祖佑（Department of Zoology, National Taiwan University）

（d） 日本学術会議地球物理学研究連絡委員会海洋物理学分科会委員候補者推薦の件

先に海洋学会より同分科会に提出した10名の候補者に対し，同分科会で行つた選考経過につき，日高会長より報告があつた。

（e） 日高会長帰国の挨拶

（f） 編集の件（宇田副会長）

○会誌16巻3号に校正の遅れた論文があつたため，発行が遅れたが年内には出る予定。

○次の二氏が本日より編集委員に追加される事が承認された。

森田　良美氏（石野委員不在のため）

梶浦欣二郎氏（吉田委員の後任として）

（g） 事務担当者の交替について

事務の富永氏が辞任を申し出たので（なるべく12月まで）早急に後任をみつける。なお，事務引きつぎの関係上，しばらくの間（最大36年3月まで）後任者と富永氏を重複雇用する。後任者の選考は会長が行う。雇用条件としては，週3日勤務，俸給月額6,000円，ボーナス2ケ月分，600円以下の交通費（公務員並）支給。

（3） 1月評議員会（1月17日，於東大）

出席者（順不同）佐々木忠義，宇田道隆，竹内能忠，丸茂隆三，日高孝次，吉田耕造，福岡二郎，増沢譲太郎　平野敏行，半沢正男。

決定・処理事項

（a） 年会及び総会の件（丸茂，半沢評議員）

本年は年会及び総会は次の通り行う。

日時　昭和36年4月20日～22日

場所　神戸市中小企業センター

（b） 評議員選挙の件（佐々木評議員）

評議員の選挙については次の計画で行う。

評議員改選についての通知，出来るだけ早く出す。

立候補及び候補者推薦届出締切り　2月13日（必着）

立候補者及び推薦候補者名公示発送　3月15日

投票締切り　4月15日（必着）

開　　票　4月18日（必着）

（c） 編集の件(宇田評議員)

会誌 16 巻4号は 10 月以内に発行予定。17巻1号までの原稿は集つているが，17巻2号分がないので，3月末位までに集めなければならない状況である。

（d） 生物環境シンポジウムの件(宇田評議員)

日時 4月8日(土) 9時～18時

場所 東京水産大学大会議室

主題 新らしい海洋学測器及び方法について

（e） 新入会員の件(丸茂評議員)

次の三氏の入会が承認された。

黒沼 新一（神戸海洋気象台）

佐々木 実（東北海区水産研究所）

高 橋 正（東京水産大学）

（f） 退職金の件(福岡評議員)

富永氏の退職金は，公務員の非常勤職員の規則を適用する事に決つた。

（g） 日本学術会議地球物理学研究連絡委員会海洋物理学分科会委員候補者推薦について

(日高会長) 上記について経過報告があつた。

（h） 海洋綜合研究所の件(日高会長)

東大理学部内の打合せ会が開かれ，吉田，奈須の両氏が，幹事として選ばれた。

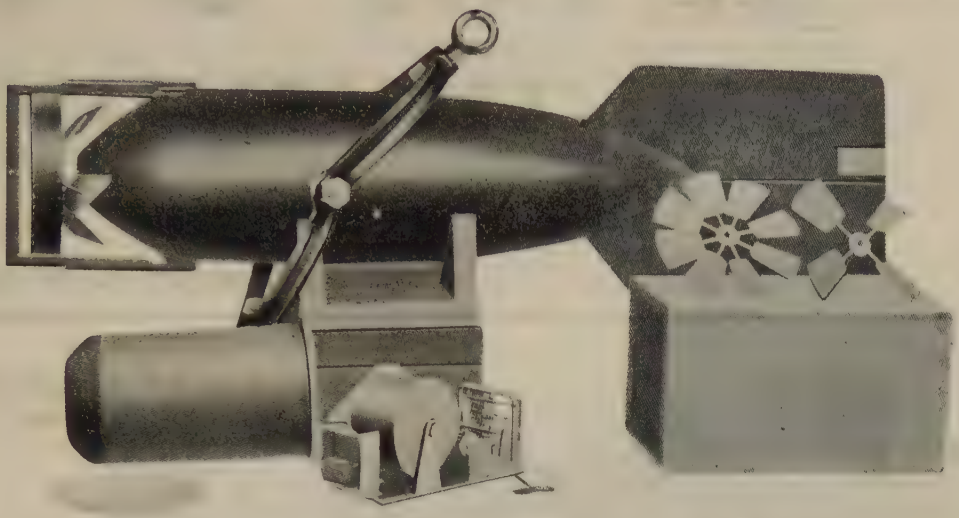
船が絶対に必要である事が強調され，同時に海の地球物理学等，例えば，地震，地磁気及び重力，海底の熱流等に関する講座が要望されているとの報告があつた。14日には大体意見がまとまり，27日に理学部，農学部合同の打合せ会を開く予定である。

（i） インド洋観測について(宇田評議員)

上記について観測計画その他について報告があつた。

（j） 太平洋学術会議について(日高会長)

上記について報告があつた。



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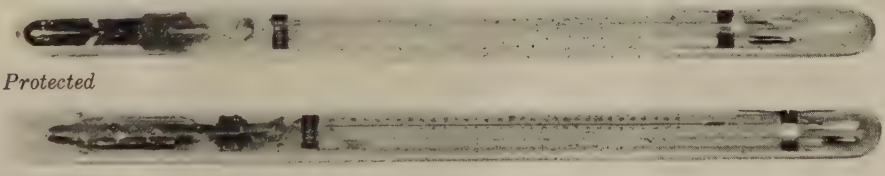

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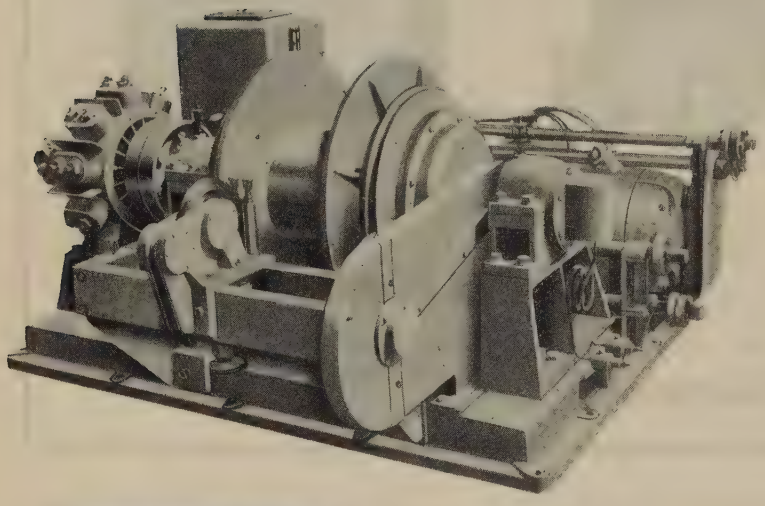

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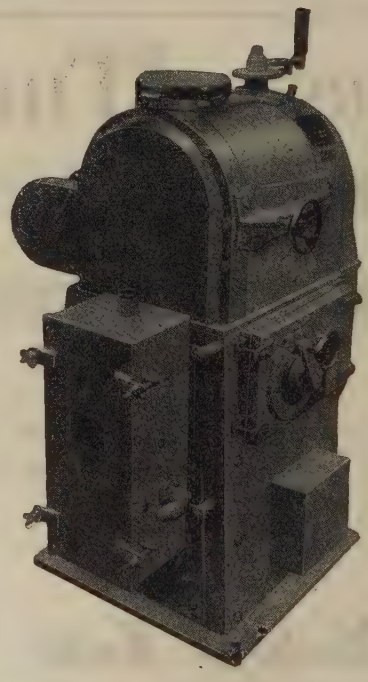
(遠 隔 操 作)

- ○ ワイヤー，テーパード
  ワイヤー 8000 m
- ○ 遠隔操作方式
- ○ A.C (D.C) 15 馬力

5P 型
捲揚機遠隔操作盤



T.S.—0 型
B.T. 用電動捲揚機

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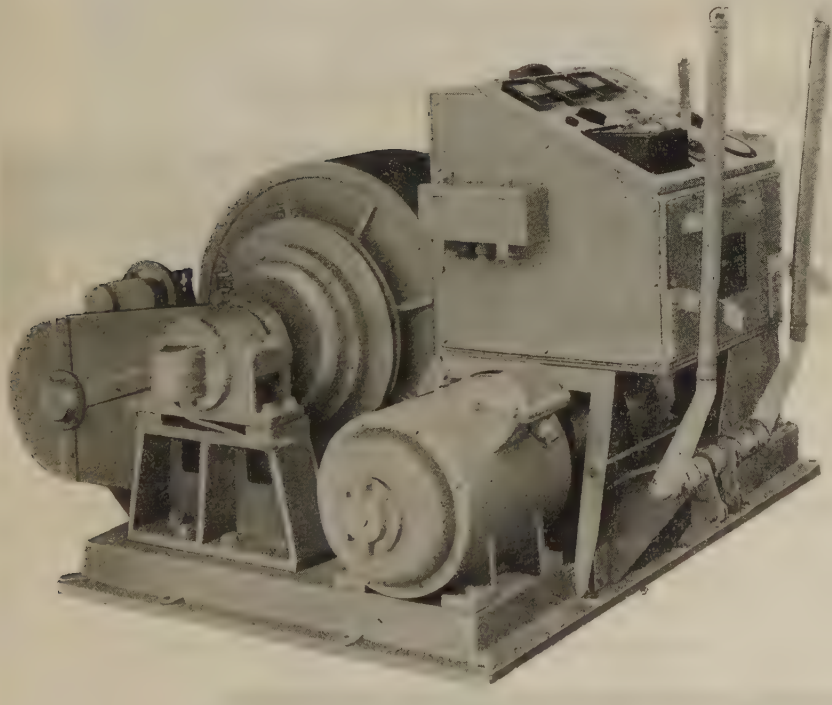

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○ ワイヤー 4 m/m
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○ A C. (D C.)
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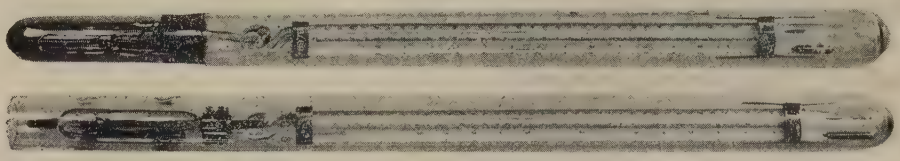

DEPTH 10,000 M

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pressure coeff. $<0.07°C/\frac{kg}{cm^2}$

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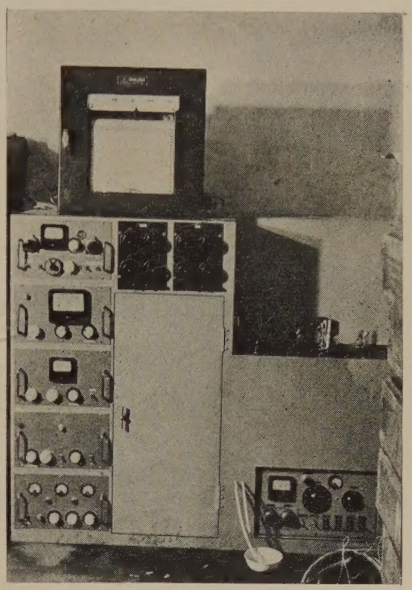
R.I.S.

RIGO-SALINOMETER

気象庁御指導　特許出願中

海水の電気伝導度を測定して塩分を算出し塩検に代える企は古からあり各所で試作されて来ましたが 1956 年 Woods Hole 海洋研究所で新しい構想のもとに電気伝導度塩分計を完成し次第に英米の塩検はこの装置を使用する方法に変りつつあります。

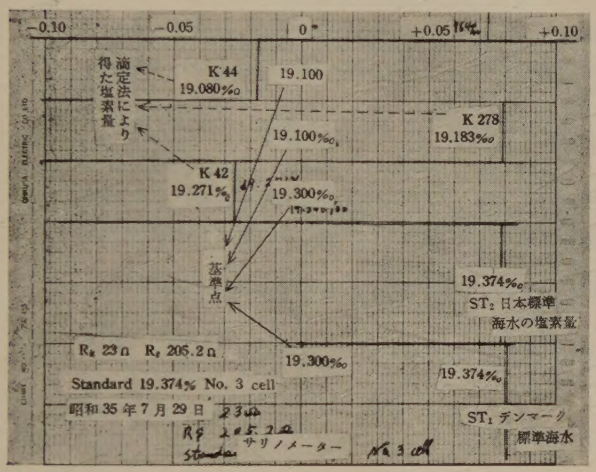
弊社に於きましてもこの度気象庁の御指導により RIGO-SALINOMETER を完成致しました。



（試　作　品）

製品としてはよりコンパクトなものを製作中です。

本装置による測定例



	塩素量	基準点	記　録	サリメーターの読み	補整値	塩素量補整値
ST₁	19.379	19.300	+0.081	19.381	19.379	0.000
ST₂	19.374	19.300	+0.078	19.378	19.376	−0.002
K42	19.271	19.300	−0.026	19.274	19.272	−0.001
K278	19.180	19.100	+0.079	19.179	19.177	+0.003
K44	19.080	19.100	−0.017	19.083	19.081	−0.001

補整値＝サリノメーターの読み＋(標準海水の塩素量−標準海水の読み)

例: K42　　19.271＝19.274＋(19.379−19.381)

＝19.274＋(−2)

基準点はサリノメーターの Cl ダイアルにて求める。

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RIGO-SALINOMETER

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